

Study of the interaction of tris-(8-hydroxyquinoline) aluminum (Alq_3) with potassium using vibrational spectroscopy: Examination of possible isomerization upon K doping

Y. Sakurai,^{a)} Y. Hosoi,^{b)} H. Ishii,^{c)} and Y. Ouchi

Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

G. Salvan, A. Kobitski, T. U. Kampen, and D. R. T. Zahn

Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

K. Seki

Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

(Received 10 February 2004; accepted 3 June 2004)

The geometrical structure of potassium-doped Alq_3 [tris-(8-hydroxyquinoline) aluminum] and the interaction between the Alq_3 molecule and potassium were studied using infrared reflection absorption spectroscopy (IRRAS), surface-enhanced Raman scattering (SERS), and density functional theory calculations. A major aim of this study was to examine the theoretically predicted isomerization of Alq_3 molecules from the meridional form to the facial form upon alkali-metal doping. The observed spectra show significant changes with the deposition of potassium on a thin Alq_3 film. The calculated IR spectra of the K- Alq_3 complex differ significantly between the meridional and facial forms, and the calculation for the meridional form agrees fairly well with the observed spectrum. This demonstrates that (1) the Alq_3 molecule does not change to a facial isomer with the deposition of potassium, but retains the meridional form, in contrast to the reported theoretical prediction, and (2) the structure of the complex as evaluated from geometry optimization is reliable. We also found that the calculated IR spectrum of the K- Alq_3 complex with Alq_3 in its meridional form is significantly different from that of the isolated anion in the same isomeric form, which probably reflects nonuniform interaction between K and the three ligands of Alq_3 . On the other hand, the calculated spectra of Alq_3 and the K- Alq_3 complex in the facial form are similar, possibly because the K atom in the suggested structure lies on the axis of threefold symmetry, leading to an equivalent effect on the three ligands. Even though vibrational spectra of alkali-metal-doped organic materials are usually interpreted on the basis of an isolated anion, the results presented here show that care should be taken in interpreting the spectra of doped organic materials without considering the presence of the counter ion. The observed SERS spectra and theoretical calculations of the Raman spectra show similar trends when compared to the IRRAS results. The present results show that vibrational spectroscopy can be used as a sensitive tool for discerning subtle differences between isomers as well as between complexes and isolated anions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1776626]

I. INTRODUCTION

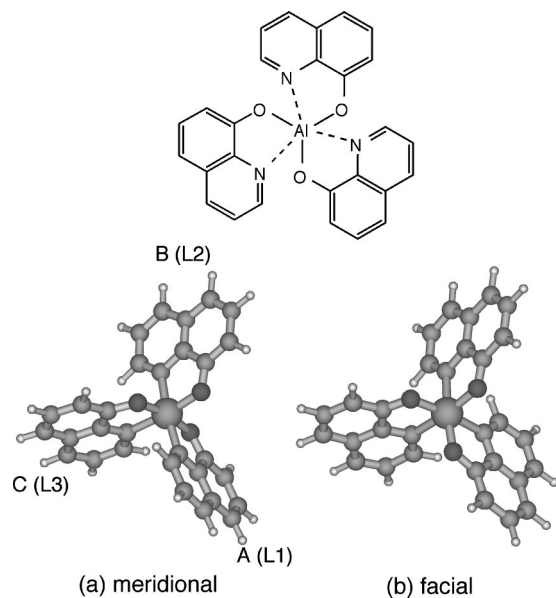
Recently, organic light-emitting diodes (OLEDs) have attracted much attention due to their potential applications in multicolor flat-panel displays. Tris-(8-hydroxyquinoline) aluminum (Alq_3) is widely used as an electron transport/light-emitting layer in such OLEDs.¹ The chemical structure of Alq_3 and two possible geometrical isomers of Alq_3 , meridional (C_1 symmetry) and facial (C_3 symmetry) forms, are shown in Fig. 1. In the meridional isomer, the three ligands are not equivalent with respect to the Al atom [Fig. 1(a)],

while they are equivalent in the facial isomer [Fig. 1(b)]. The names of the ligands A–C and L1–L3 for the meridional isomer in Fig. 1 are those used in Refs. 2 and 3, respectively. It has been reported that the meridional isomer is the dominant species in most cases, such as in amorphous evaporated films in the Ar-matrix-isolated state and crystalline states prepared under ambient conditions.^{4,5} Theoretical calculations by DFT (density functional theory) using the BLYP/ECP (Ref. 3) and B3LYP/SDD (Ref. 5) methods also predict that the meridional isomer is more stable than the facial isomer by 4–8 kcal/mol. Even though in this work we only used Alq_3 in the meridional form as the starting material for sample preparation, German and Italian groups^{6–8} have recently reported that the facial isomer has been successfully isolated in pure form. Further experiments using this isomer will expand our basic knowledge about this important material.

^{a)}Present address: UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan; FAX: +81-564-54-7079; electronic mail: sakurai@ims.ac.jp

^{b)}Present address: Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan.

^{c)}Present address: Research Institute of Electrical Communication, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan.

FIG. 1. Chemical structure and geometrical isomers of Alq₃.

A typical OLED consists of indium tin oxide as the anode on which organic thin films are sequentially deposited, with low work function metals finally deposited as the cathode. Since the properties of the metal/organic interface affect the performance of such devices, an understanding of the interaction between such low work function metals and organic molecules is important. Hence, the interfaces between Alq₃ and metals such as Al, Mg, Ca, Li, and K have been investigated both experimentally and theoretically.^{2,9–18} It has been reported that charge transfer mainly takes place between Alq₃ and alkali metals such as K and Li, while Mg and Al form more covalent metal-carbon bonds.^{9,10}

In this paper, we will focus on the former case of alkali metals. Johansson *et al.*² studied the electronic structure of Alq₃ upon doping with potassium and lithium using a combination of x-ray and ultraviolet photoelectron spectroscopy. They also performed quantum-chemical calculations for the K-Alq₃ complex using the DFT/BLYP method, assuming that Alq₃ was in the meridional form. They concluded that (1) a negative charge is transferred from metal atoms to the nitrogen atoms (0.866e for the 1:1 K complex determined from the DFT calculation, and slightly less for the Li complex, as judged from their XPS spectra), (2) the potassium atom interacts mainly with the nearest neighboring ligand [A in Fig. 1(a)], (3) there is a weaker interaction with the next nearest neighboring ligand [B in Fig. 1(a)], (4) the change in the valence states observed in the UPS spectra is similar for both K and Li complexes, (5) the transferred charge is mainly localized on one of the ligands (A) (0.63e), with a smaller fraction on B, and (6) the calculated highest occupied molecular orbital (HOMO) of the K complex is essentially the same as the lowest unoccupied molecular orbital (LUMO) of Alq₃.

On the other hand, Curioni and Andreoni¹⁷ performed DFT calculations for the meridional and facial isomers of Alq₃ and also for Li-Alq₃, Al, and Ca complexes that included these two isomers. The results indicated that the facial

isomer is more stable than the meridional isomer by at least 10 kcal/mol in these metal complexes. Thus, they suggested that molecules in the meridional form in the neutral state may be converted into the facial isomer upon complexation. They also concluded that although complete electron transfer from lithium takes place, the charge distribution in the Alq₃ part of the complex differs from that in an isolated radical anion, although the excess electron is also localized on the pyridyl side of the ligands.

Thus, although previous studies have clarified many important points, it is desirable to obtain even more experimental information on the nature of the Alq₃ molecule in an alkaline metal complex. Important questions still remain, such as (1) which isomeric form do the doped Alq₃ molecules take? (2) to what extent can we regard the Alq₃ anion in the Alq₃ complex as being similar to an isolated anion? and (3) which part of the Alq₃ molecule is affected by the metal atom? The importance of the possible conversion from the meridional to the facial isomer was also stressed by Kushto *et al.*⁵ Since the calculations by Curioni *et al.*³ showed that the facial isomer is more efficient as an electron trap, the possible formation of facial isomers by metal deposition may govern charge transport in the bulk material. Thus, possible isomerization in the complexes is important in devices using Alq₃.

To clarify these points and to obtain a deeper insight into metal-Alq₃ interaction, we studied the geometrical structure of potassium-doped Alq₃ films and the interaction between Alq₃ and potassium using infrared reflection absorption spectroscopy (IRRAS), surface-enhanced Raman scattering (SERS), and DFT calculations. Such vibrational spectroscopic studies of potassium doping of Alq₃ films have not been reported previously. It is well known that IR spectroscopy and Raman spectroscopy are complementary to each other in many aspects, such as selection rules. In IRRAS, high sensitivity is achieved by the glazing reflection geometry, and in SERS, the extensive enhancement of Raman scattering is caused by silver clusters. Both techniques are powerful probes for examining the structure and chemistry of the surface and interface due to their high sensitivity and resolution.

The assignment of vibrational modes of Alq₃ has been reported by various workers using IR and Raman spectroscopy and theoretical calculations.^{5,19,20} These studies have already established the assignments of the meridional form of Alq₃, which has been the form predominantly observed in all these studies. In this work, we extended these studies to the K-Alq₃ complex. The results show fairly good agreement between the observed and calculated IR spectra, which demonstrates that DFT calculations are useful for such complex molecular systems. The results not only clarify the isomerism but also provide useful information regarding other factors, such as questions (2) and (3) described above.

II. EXPERIMENTAL AND THEORETICAL

The IRRAS and SERS experiments were performed on layers grown on Ag(111) surfaces, prepared on Si substrates in ultrahigh vacuum (UHV) chambers (base pressure <4

$\times 10^{-8}$ Pa). The *p*-type Si(111) substrate was cleaned by dipping in acetone, ethanol, and deionized water in an ultrasonic bath. The substrate was then dipped in 40% HF solution for 2 min,²¹ and immediately transferred to a UHV chamber. A 1×1 low energy electron diffraction (LEED) pattern indicated the formation of a hydrogen-terminated Si(111) surface. Ag films, 100 nm thick, were deposited on this hydrogen-terminated Si(111) surface from a Knudsen cell. LEED and Auger measurements revealed the formation of a clean Ag(111) surface. The sample of Alq_3 was supplied by Aldrich and purified by sublimation. Alq_3 films were prepared by vacuum evaporation from a separate Knudsen cell onto these Ag(111) surfaces, which were kept at room temperature. The thickness of the Alq_3 film was monitored using a quartz microbalance and limited to 10 nm for IRRAS measurements or 3 nm for Raman measurements. Potassium was deposited on Alq_3 films from a SAES getter source.

IRRAS spectra were measured at Nagoya University using an IRRAS system consisting of an FT-IR spectrometer (FM—Fourier transform) (Mattson R/S-1), a mercury cadmium telluride (MCT) detector, and a UHV chamber. The spectra were obtained in single reflection mode with *p*-polarized light through a BaF_2 window and at an angle of incidence of 80° relative to surface normal. The reflected light was detected with the MCT detector. The spectra were measured in the region of $1000\text{--}4000\text{ cm}^{-1}$. IRRAS measurements below 1000 cm^{-1} were difficult to obtain using this system due to the limited sensitivity of the MCT detector. The results of 500 or 1000 scans with a resolution of 4 cm^{-1} were averaged. The complementary spectrum of Alq_3 powder was also measured for KBr pellets under ambient conditions at $400\text{--}4000\text{ cm}^{-1}$.

Raman spectra were measured at TU Chemnitz using a triple monochromator (Dilor XY) with a charge-coupled device detector that was optically aligned to the UHV chamber. The 530.9 nm line of a Kr⁺ laser was used for excitation. The laser beam (power $<30\text{ mW}$) was focused on a spot of about $300\text{ }\mu\text{m}$ in diameter on the sample surface. The spectral resolution was 2.5 cm^{-1} . To obtain strong Raman signals by surface enhancement, silver was deposited to an average thickness of 1 nm on Alq_3 films from a Knudsen cell following potassium deposition.

DFT calculations were carried out with GAUSSIAN 98 using the B3LYP functional and 6-31G(d) basis set. The geometries of the Alq_3 molecule and the $\text{Alq}_3\text{-K}$ complex were optimized by B3LYP/6-31G(d) using the optimized geometries for Alq_3 and the $\text{Alq}_3\text{-Li}$ complex reported by Curioni and Andreoni¹⁷ as the starting geometries. Since the calculated frequencies were larger than those observed in the high frequency region and smaller than those in the low frequency region, the calculated values were multiplied by 0.961 and shifted to a higher wave number by 14 cm^{-1} . Simulated spectra were obtained by convoluting the bars with heights proportional to the calculated intensities by a Lorentzian function with a full width at half maximum of 4 cm^{-1} (IR) and 2.5 cm^{-1} (Raman). The assignments of vibrational modes were made using visualized vibrational patterns.

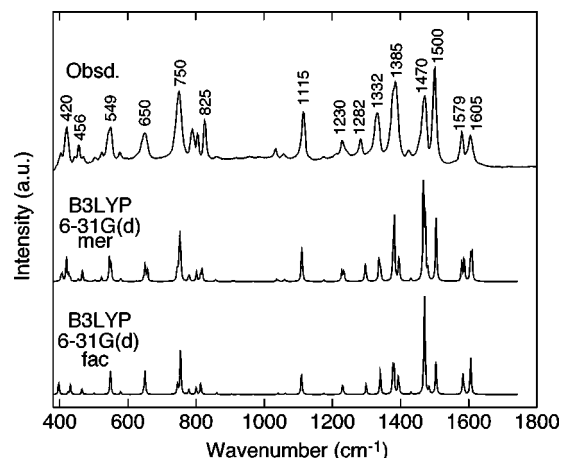


FIG. 2. Experimentally observed IR spectrum and theoretically simulated IR spectra of the meridional and facial isomers of Alq_3 .

III. RESULTS AND DISCUSSION

A. Assignments of vibrational modes of Alq_3

Figure 2 shows the experimentally observed and theoretically calculated IR spectra of Alq_3 . The theoretical spectra after scaling and shifting are shown for both meridional and facial isomers. The experimentally observed spectrum agrees well with those reported by Halls and Aroca,¹⁹ Kushto *et al.*,⁵ and Esposti *et al.*²⁰ The high-resolution-electron-energy-loss-spectroscopy (HREELS) spectrum of pristine Alq_3 film reported by He *et al.*¹³ reasonably corresponds in terms of the energies of the spectral features to the IRRAS spectrum, though the relative intensities of peaks are different. Our calculated spectra are similar to those reported by Kushto *et al.* using B3LYP/SDD DFT calculations, except for a slightly better agreement with the experimental spectrum for the intensity of the bands at 1110, 1298, and 1336 cm^{-1} . The observed spectrum agrees well with the calculation for the meridional isomer. The simulated spectrum for the facial isomer differs from the calculated and measured spectra for the meridional isomer in several respects: (1) the intensity of the bands at 1385 and 1500 cm^{-1} is weaker, and (2) the frequencies and degeneracy of the bands between 400 and 430 cm^{-1} and between 540 and 660 cm^{-1} originating from the Al-N and Al-O stretching vibrations are different, due to the higher symmetry of the facial isomer. As described in the extensive study by Kushto *et al.*,⁵ these results confirm that the Alq_3 films consist predominantly of the meridional isomer, as in various forms of crystals.²²

Assignments of the vibrational modes of Alq_3 , as deduced by comparison with the calculation, are listed in Table I, which also shows the results of Raman measurements. The modes between 1033 and 1605 cm^{-1} are mainly due to ring stretching and CH bending vibrations of the ligands, although CN stretching (1228 cm^{-1}) and CO stretching (1282 cm^{-1}) are also observed in this region. These assignments agree almost completely with those reported by previous workers.^{5,19,20} The band at 917 cm^{-1} , due to an Al-N stretching vibration, is not observed in the IR spectrum, but is weakly observed in the Raman spectrum. We will use these assignments later when discussing the change in the spectra induced by K doping.

TABLE I. Assignments of the vibrational modes of Alq_3 based on a B3LYP/6-31G(d) calculation. The listed frequencies were obtained by multiplying the original calculated values by 0.961 and shifting to a higher frequency by 14 cm^{-1} .

Calculated	Observed-spanner		Assignments
	IR	Raman	
1606	1605		Ring str.
1589		1588	Ring str., CH bend
1583	1579		Ring str.
1502	1500	1495	CH bend, ring str.
1467	1470	1465	CH bend, ring str.
1430	1424	1419	CH bend, ring str.
1381	1385	1388	Ring str.
1336	1332	1328	CH bend, ring str.
1298	1282	1282	CH bend, ring str., CO str.
1232	1228	1226	CH bend, CN str.
1222	1211	1215	CH bend, ring str.
1175	1174	1169	CH bend
1139	1134	1132	CH bend
1110	1115	1113	CH bend, ring str.
1060	1057	1053	CH bend, ring str.
1039	1033	1029	CH bend, ring str.
909		917	AlN str., ring def.
858	859	859	CH wag
816	825	822	CH wag
801	804	804	Ring def.
779	789	786	CH wag
752	750	753	Ring breathing
653	650	644	Ring def., AlO str.
624		623	Ring torsion. AlO str., AlN str.
597		592	Ring def.
577	577	575	Ring def., AlOC bend
546	549	542	Ring def., AlO str.
523	523	525	Ring def., AlO str.
506	507		Ring def.
502	502	504	Ring def.
467	470	469	Ring torsion
454	456	458	Ring torsion
429			Ring def., AlO str.
419	420	422	AlN str., AlOC bend
407	403	408	Ring def., AlOC bend
403		398	Ring def., AlN str.
356		356	Ring def., AlN str.
311		307	Ring torsion
292		293	Ring torsion

Figure 3 shows the SERS spectrum of an Alq_3 film, with silver deposited at an average thickness of 1 nm compared with the calculated Raman spectra of meridional and facial isomers. The deposition of silver led to a pronounced increase in the intensity of Raman scattering due to the SERS effect. The frequencies and relative intensities of the Alq_3 vibrational modes were not modified by Ag deposition, indicating the absence of strong chemical interaction between Ag and Alq_3 .²³ The experimentally observed spectrum in Fig. 3 agrees well with those reported by Halls and Aroca¹⁹ and Esposti *et al.*²⁰ (both with excitation at 1064 nm). However, the intensity distributions are different, which can be ascribed to the difference in excitation energy. The numerical data and assignments are listed in Table I. The simulated spectra of both meridional and facial isomers show compa-

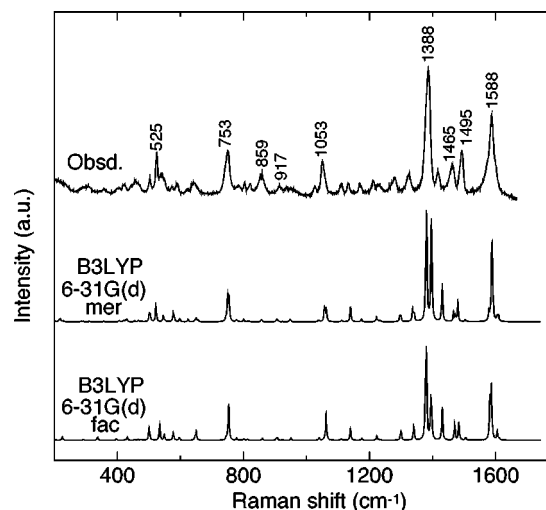


FIG. 3. SERS spectrum of Alq_3 film with a 1 nm thick deposition of silver and simulated Raman spectra of the meridional and facial isomers of Alq_3 .

table agreement with the experimental spectrum. The reported simulated spectrum for the facial isomer, using the Hartree-Fock 6-31G* calculation,¹⁹ differs slightly from the experiment with regard to the intensity distribution. The frequency of the mode due to the Al-O stretching vibration observed at 525 cm^{-1} agrees slightly better with the value (523 cm^{-1}) calculated for the meridional isomer than that (534 cm^{-1}) calculated for the facial isomer. Thus, while it is difficult to identify the predominant isomer from Raman spectroscopy, the results do not contradict the predominance of the meridional isomer deduced from IRRAS spectroscopy.

B. Changes in IRRAS and SERS spectra with potassium doping

Figure 4 shows the IRRAS spectra of a clean Alq_3 film and after three successive steps of potassium evaporation. Upon potassium evaporation, most of the vibrational bands between 1000 and 1606 cm^{-1} become weaker, and new bands (shown with *) appear at 1082, 1208, 1272, 1296, 1300, 1387, 1425, 1452, 1500, 1552, 1579, and 1606 cm^{-1} .

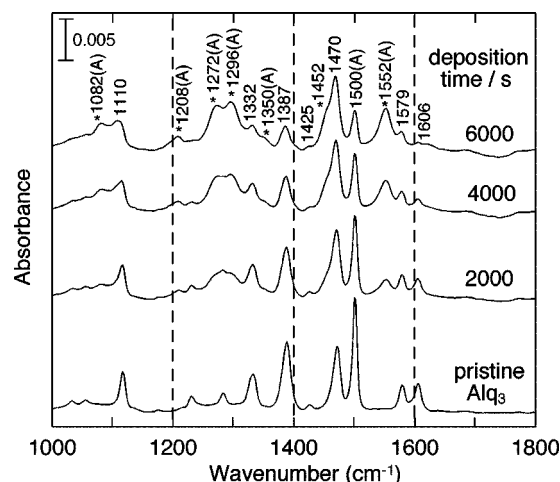


FIG. 4. Changes in the IRRAS spectra of a clean Alq_3 film upon potassium deposition. New bands are marked with asterisks (*). The bands assigned to the vibrational modes in ligand A are marked with (A) after the wave number values.

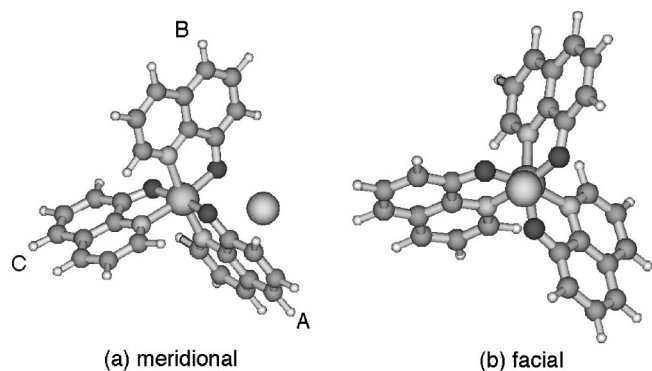


FIG. 5. Optimized geometry of the meridional and facial isomers of K-Alq₃ complex.

1350, 1452 (shoulder), and 1552 cm⁻¹. These bands are in the region of the ring stretching and CH bending modes of the quinoline ligands. The IRRAS spectra did not change further with potassium deposition in excess of 6000 s.

The reported UPS, XPS, and theoretical studies for K-Alq₃ and Li-Alq₃ complexes have indicated electron transfer from the alkali metal to Alq₃.^{2,17} The amount of charge transfer from the K atom to meridional Alq₃ molecule in a 1:1 complex was theoretically estimated by Johansson *et al.* to be 0.866e.² In addition to these results, our recent near-edge x-ray-absorption fine structure (NEXAFS) investigations revealed a decrease in intensity for core excitation to the π^* LUMO after potassium deposition.²⁴ This also indicates electron transfer from potassium to the LUMO of Alq₃.

As mentioned above, geometry optimization was carried out starting from a geometry similar to that reported by Curioni and Andreoni,¹⁷ with the resulting geometries similar to those at the start. They are shown in Fig. 5. In the facial isomer, the K atom is on the axis of threefold symmetry. On the other hand, in the meridional isomer, the K atom lies between ligands A and B. The changes in the Al-O and Al-N bond lengths are shown in Table II. The calculated amount of electron transfer from the K atom to the Alq₃ molecule is 0.70e and 0.75e for the meridional and facial forms, respectively, and the value for the meridional form is smaller than that reported by Johansson *et al.* (0.866e).² The charge distribution in the two isomeric forms is depicted in Fig. 6. The K atom is shown by a cross (+), and the values for the K, Al, N, and O atoms are shown in bold. The values in parentheses indicate the change in charge from isolated Alq₃ and K to the K-Alq₃ complex. The charge on hydrogen atoms, omitted in Fig. 6, is 0.10–0.20 (–0.03 to 0.01) for the

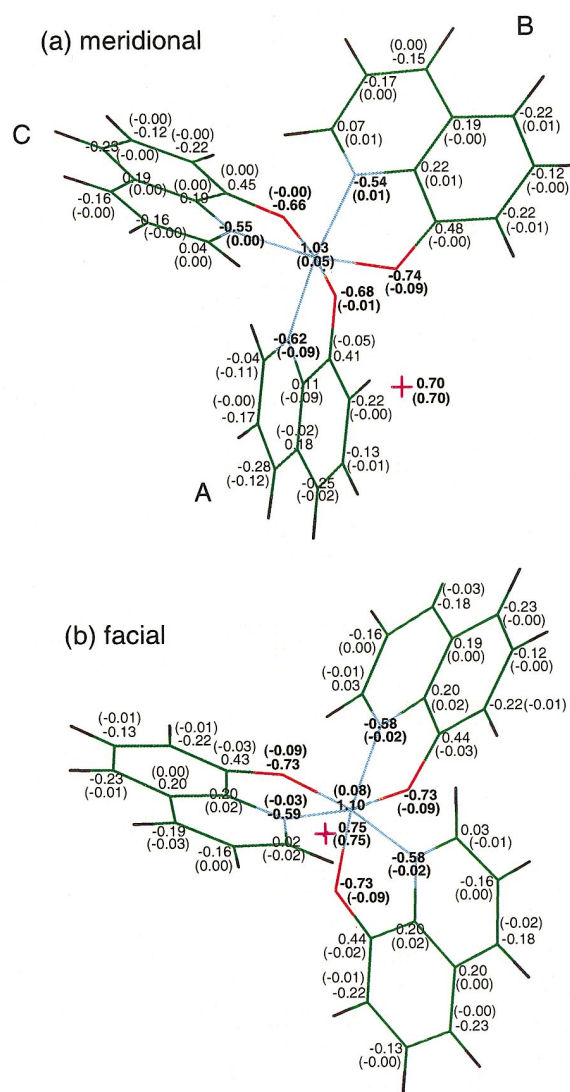


FIG. 6. (Color) Charge distribution in the meridional and facial isomers of K-Alq₃ complex.

meridional isomer and 0.11–0.16 (–0.03 to 0.00) for the facial isomer. We see that the distribution is equal among the three ligands for the facial isomer, reflecting its threefold symmetry. On the other hand, the excess electron in the meridional isomer is mostly localized on ligand A (A, –0.65e; B, –0.08e; C, –0.02e), reflecting inequality among the ligands. More specifically, it is concentrated at the N and C atoms in the pyridyl part of ligand A, and at the O atom in ligand B. This agrees with the results by Johansson *et al.*² for the meridional isomer, where the excess electron predominantly occupies the LUMO at ligand A and the pyridyl part in this ligand.

The charge distributions in an isolated anion in both isomeric forms are also shown in Fig. 7. The values in parentheses indicate the difference in charge from Alq₃ to Alq₃ anion. The charge distribution on hydrogen atoms is 0.07–0.18 (–0.06 to –0.01) for the meridional isomer and 0.08–0.15 (–0.05 to –0.01) for the facial isomer. Based on these results for the anions and the complex, we can examine

TABLE II. The calculated bond lengths of Alq₃ (mer) and K-Alq₃ (mer). The values in bold indicate large changes.

Bonds	Alq ₃	K-Alq ₃
Al-O(A)	1.8946	1.8814
Al-O(B)	1.8667	1.9359
Al-O(C)	1.8960	1.9019
Al-N(A)	2.0276	1.9538
Al-N(B)	2.0539	2.0660
Al-N(C)	2.0644	2.0385

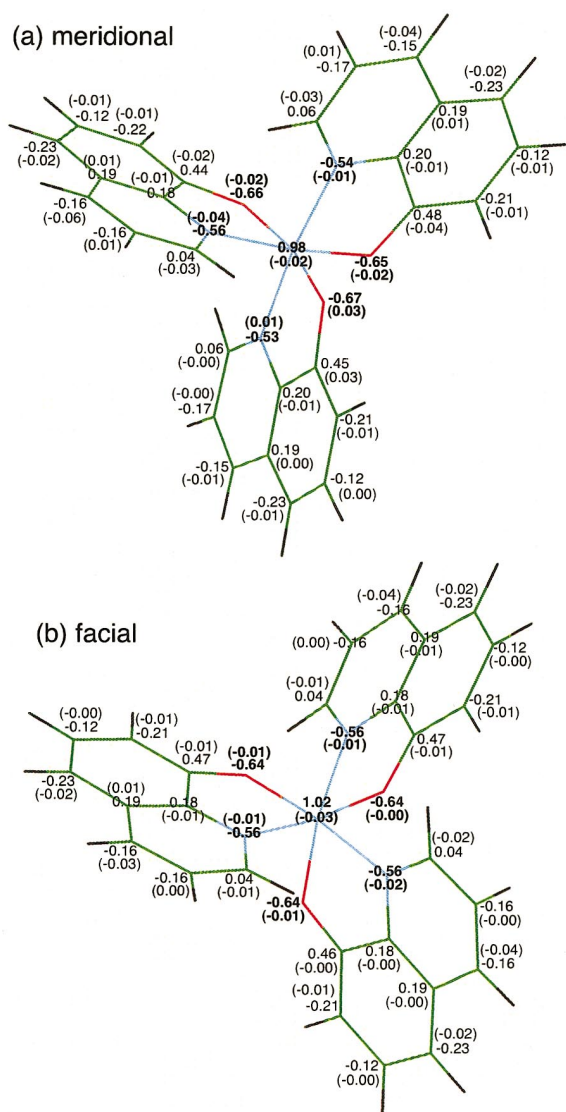


FIG. 7. (Color) Charge distribution in the meridional and facial isomers of Alq_3 anion.

the extent to which the Alq_3 part in the K complex is similar to an isolated anion in terms of vibrational spectroscopy, as discussed below.

In Fig. 8, we compare the simulated IR spectra for the complex and isolated anion of the meridional and facial isomers, together with the observed IRRAS spectrum. They show various degrees of similarity and divergence. First, we note the similarity between the complex and the isolated anion of the facial isomer. We may ascribe this to the preservation of threefold symmetry, with the K cation having an equal effect on the three ligands. The charge distribution of the Alq_3 part in the complex is almost the same as that in the isolated anion, except for the small change at the oxygen atoms. Moreover, the excess charge is also distributed almost equally among the ligands in both neutral Alq_3 and the complex.

The simulated IR spectrum of the isolated anion of the meridional isomer is different from those of the facial species described above. In this isomer, the distribution of elec-

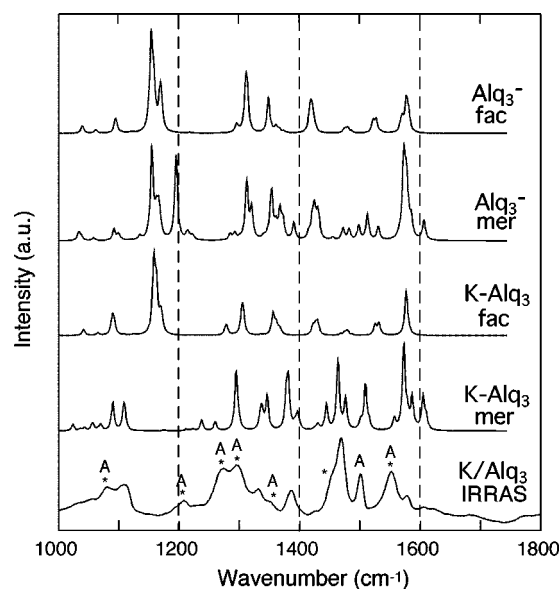


FIG. 8. Simulated IR spectra for the K complex and isolated anion with the meridional and facial isomers of Alq_3 , together with the experimental IRRAS spectrum. New bands are marked with asterisks (*). The bands assigned to the vibrational modes in ligand A are marked with (A).

trons is uneven among the ligands (A, $-0.11e$; B, $-0.48e$; C, $-0.38e$), which results in a spectrum that is significantly different from that of the facial isomer.

Again, the simulated IR spectrum of the K- Alq_3 complex in the meridional form is significantly different from that of the isolated anion and also from that of the anion and K complex in the facial isomer form. The presence of the K ion significantly modifies the electron distribution among the ligands (A, $-0.65e$; B, $-0.08e$; C, $-0.02e$), as described above. The major distribution is shifted from C to A, which is understandable since A is the nearest neighboring ligand to the K^+ ion. The distribution within the ligands is also very different from those in the isolated anion, in particular in ligand A. Therefore, we can confirm that a potassium-doped meridional Alq_3 molecule is in a completely different state than an isolated Alq_3 anion from the perspective of molecular vibrations. As for the difference in the distribution of the excess charge compared to the neutral Alq_3 molecule, the excess charge in the K complex is concentrated at the N and C atoms in the pyridyl part of ligand A, and at the O atom in ligand B. In the isolated anion, the variation in the excess charge distribution among ligands is smaller than that in the K complex.

In Fig. 8, the observed IRRAS spectrum agrees well with the simulated spectrum of the K- Alq_3 complex of the meridional isomer. In particular, we note (1) the appearance of a doublet at 1100 cm^{-1} , (2) the absence of a strong peak at around 1150 cm^{-1} , and (3) reproduction of the intense peaks at 1470 cm^{-1} and 1500 cm^{-1} . On the other hand, other simulated spectra show much worse correspondence with the observed spectrum. Thus, we can conclude that Alq_3 molecule does not change to the facial isomer upon the deposition of potassium but remains in the meridional form. Although this alone does not contradict the predicted conversion for the Li complex reported by Curioni and Andreoni,¹⁷ the similarity

TABLE III. Assignments of the vibrational modes of K-Alq₃ based on a B3LYP/6-31G(d) calculation. Calculated frequencies were multiplied by 0.961 and shifted to a higher frequency by 14 cm⁻¹. Three ligands of Alq₃ are labeled A, B, and C. Ligand A corresponds to the ligand closest to the potassium atom, and ligand B corresponds to the ligand second closest to the potassium atom.

Calculated	Observed-spanner		Assignments (ligands)
	IR	Raman	
1608	1606		Ring str. (C,B)
1586	1579	1586	Ring str. (B,C)
1572		1572	Ring str. (A,C)
1556	1552		Ring str., CH bend, CO str. (A,C)
1514		1533	CH bend, ring str. (A)
1487	1500	1493	Ring str., CH bend (B,A,C)
1467	1470	1454	CH bend, ring str., CO str. (C)
1428	1425	1417	CH bend, ring str. (B)
1374	1387	1383	Ring str., CH bend (B,C)
1336	1350	1347	Ring str., CH bend, CO bend (A)
1337	1332		CH bend (B,C)
1295	1296	1280	CH bend, CO str., ring str. (A)
1277	1272	1267	CH bend, ring str. (A)
1224		1227	CH bend, ring str. (C)
1211	1208	1211	CH bend, ring str. (A)
1180		1199	CH bend, ring str. (A)
1141		1137	CH bend, ring str. (B)
1108	1110	1110	CH bend, ring str., AlN str. (C,B)
1090	1082	1083	CH bend, ring str., AlN str., CO str. (A)
1058		1051	CH bend, ring str. (A,C)
1023		1026	CC str., CH bend (A)
905		902	AlN str. (B,C)
853		861	CH wag (C)
819		822	CH wag (A)
789		792	Ring def. (A)
745		743	CH def., AlO str. (A,C)
647		644	CH wag (A)
579		589	Ring def., AlOC bend (C)
569		573	Ring torsion (A)
504		505	Ring def. (B,C), ring torsion (A)
466		469	Ring torsion (B,C)
461		458	Ring torsion (B,C)
426		423	Ring torsion, AlN str. (A,B,C)
402		399	Ring def. (B,C), ring torsion (A)
361		369	Ring torsion (A), AlN str. (C)
305		296	Ring torsion (B,A)
211		207	Ring torsion (C)

of the ultraviolet photoemission spectroscopy and x-ray absorption spectroscopy results for the Li and K complexes suggests that conversion is also unlikely for Li-Alq₃. The total energies of the meridional isomer of K-Alq₃ complex calculated here show that the facial isomer is 5.5 kcal/mol more stable than the meridional isomer. This contradicts the experimental observation, although the energy difference is smaller than that estimated in Ref. 17 (>10 kcal/mol), and further study is needed.

Assignments of the vibrational modes of K-doped Alq₃, deduced by comparing the IRRAS spectra with the calculation, are listed in Table III. Most of the new bands that appear upon K deposition can be assigned to the vibrational modes, with the main contribution from ligand A, which is

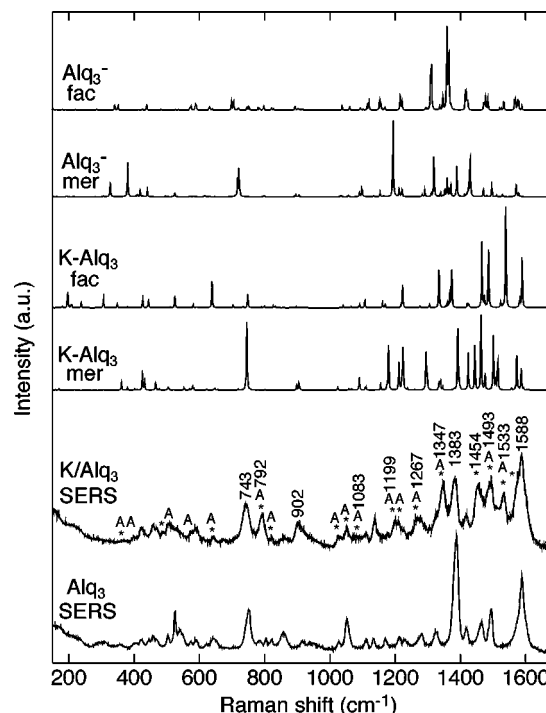


FIG. 9. SERS spectra of Alq₃ film before and after potassium deposition and simulated Raman spectra for the K complex and isolated anion with the meridional and facial isomers of Alq₃. New bands are marked with asterisks (*). The bands assigned to the vibrational modes in ligand A are marked with (A).

closest to the potassium atom. These bands from ligand A are marked with (A) after the wave number values in Fig. 4 and at the peaks in Fig. 8.

Figure 9 shows the SERS spectra of an Alq₃ film before and after potassium deposition. The region from 1000 to 1600 cm⁻¹ shows the vibrational modes of the quinoline groups. After K deposition, the relative intensities of the vibrational modes in this region change and new bands appear at 1083, 1199, 1267, 1347, 1454, and 1533 cm⁻¹. In the region below 1000 cm⁻¹, which could not be measured by IRRAS, new bands appear at 369, 488, 674, 743, 792, and 902 cm⁻¹. These new bands are marked with * in Fig. 9. We consider that most of the Alq₃ molecules react with K, since the bands associated with pristine Alq₃, for example, the band at 525 cm⁻¹, become very weak after K deposition.

For comparison with these observed data, we also calculated the Raman spectra of the meridional and facial isomers of the K-Alq₃ complex and an isolated anion. In Fig. 9, these are compared with the experimentally observed SERS spectrum. As in the case of IR, there are major differences in the calculated Raman spectra. The spectra of the facial Alq₃ anion and the facial K-Alq₃ complex are somewhat similar concerning energies, possibly because both have threefold symmetry as mentioned above. The relative intensity of the bands in the observed spectrum does not agree well with the simulated spectra even for the K complex with the meridional isomer of Alq₃. This is probably due to the effect of a resonance of the Kr⁺ laser (530.9 nm) with visible absorption induced by K doping, which is expected to appear in a similar region as the broad peak observed for Li-Alq₃ complex at 615 nm with a full width at half maximum of about

200 nm.²⁵ This hinders the detailed analysis of the SERS spectra. Nevertheless, we made tentative assignments of the bands by comparison with the calculated spectrum for the meridional form of K-Alq₃ complex, based only on the correspondence of energy positions, without considering the intensities (Table III). In the high frequency region, the new bands at 1083, 1267, and 1347 cm⁻¹ seem to correspond to the new bands in the IR spectra at 1082, 1272, and 1350 cm⁻¹, which are assigned to vibrations mainly at ligand A. Other bands at 1199 and 1533 cm⁻¹ can also be assigned to vibrations at ligand A. These are marked with * in Fig. 9.

The band assigned to the Al-O stretching mode at 525 cm⁻¹ becomes weak upon potassium deposition and the band assigned to the Al-N stretching mode at 917 cm⁻¹ strengthens and is shifted to 902 cm⁻¹. This suggests that the environment in the region of the Al-O and Al-N bonds is changed by potassium doping. The shift of the Al-N stretching mode to a lower frequency indicates that the Al-N bond weakens with potassium doping. If the LUMO of Alq₃, where the transferred electron sits, has an antibonding character at the Al-N bond, where the transferred electron resides, the Al-N bond becomes weak. Based on the DFT calculation, the LUMO orbital is localized on the quinoline ligand, but not on the Al atom. Hence, it is difficult to explain the shift of the Al-N stretching mode to a lower frequency in terms of the LUMO character and such variation requires further study.

He *et al.*¹³ reported HREELS spectra of the Mg/Alq₃ interface. After Mg was deposited on the Alq₃ layer, the HREELS spectra showed changes such as a decrease in intensity and broadening and shifting of peaks, and became more complicated. These trends are similar to the presently observed results of IRRAS and SERS of K-doped Alq₃. However a detailed comparison was difficult due to the poor resolution of HREELS and the large difference in relative intensities between HREELS and other spectra even for pristine Alq₃.

The present results permit a few general comments on the usefulness of vibrational spectroscopy in the study of such electronically functional organic molecular systems. First, vibrational spectroscopy could be used effectively for the discrimination of possible isomers. This is due to the large difference in the effect of the K⁺ ion on the two isomers, in particular the preservation of high symmetry in the facial isomer and the lack of equivalence of the ligands in the meridional isomer, which leads to the predominance of ligand A. Second, the good agreement between the observed and simulated IR spectra of the K-Alq₃ complex demonstrates that the spectrum of such a complex system can still be fairly well interpreted when geometry optimization is properly used. Third, the calculated spectra indicate that the vibrational spectra of the K-Alq₃ complex are very different from those of the isolated anion. This shows that care should be taken in interpreting the spectra of doped organic materials without considering the presence of the counter ion.

Finally, we will examine the possibility of discriminating among the chemical species examined above by photoelectron spectroscopy, since this shows the advantages/disadvantages of vibrational spectroscopy. Figure 10 depicts

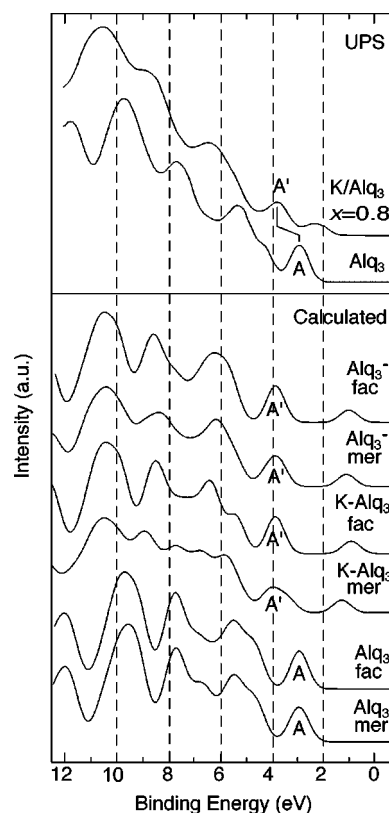


FIG. 10. Comparison of the observed UPS spectra (Ref. 18) and calculated density of states. The calculated curves have been scaled and shifted to align with the experimental results at peaks A (neutral) and A' (anion and complex), which correspond to the HOMO of neutral Alq₃.

the calculated density of states (DOS) for the two isomers of the isolated anion and the K-Alq₃ complexes and also the observed spectra reported by Schwieger *et al.*¹⁸ (which are very similar to the spectra reported by Johansson *et al.*²). The DOS of the K-Alq₃ complexes for the two isomers are not very different and there is also only a slight difference between the calculated DOS of the complex and isolated anion. Considering the generally limited correspondence between the simulation and the observed spectra, it is difficult to distinguish the subtle difference between the four states of Alq₃. This highlights that vibrational spectroscopy is a highly sensitive tool for discriminating subtle differences between the isomers and between the complex and isolated anion.

IV. CONCLUSION

The geometrical structure of the potassium-doped Alq₃ molecule and the interaction between Alq₃ and potassium were studied using IRRAS, SERS, and DFT calculations. In contrast to previous theoretical predictions, we found that the Alq₃ molecule does not change to the facial isomer upon the deposition of potassium, but rather maintains the meridional form. This conclusion is based on the large difference between the calculated IR spectra of the K-Alq₃ complex for the meridional and facial isomers and the good correspondence of the former with the observed spectra. These calculations also confirm the conclusion of previous researchers² that the change in electron density from the neutral molecule is concentrated on the ligand nearest the potassium atom, and

in particular the pyridyl part within this ligand. The calculated vibrational spectra of potassium-doped Alq_3 were very different from those of the isolated anion. This indicates that care should be taken in interpreting the spectra of doped organic materials without also considering the presence of the counter ion, although the vibrational spectra of doped organic materials are usually interpreted by considering an isolated anion-cation model. The SERS results and corresponding calculations provide information about the complex, although a detailed analysis was hindered probably due to the effect of resonance induced by K doping. We also showed that vibrational spectroscopy can be a more sensitive tool than UPS for identifying subtle differences between the isomers. Although the experimental results obtained here were all predominantly related to the meridional isomer, the calculated results for the facial isomer should also be useful for possible future experiments using facial isomers.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the EU-funded Human Potential Research Training Network DIODE (Contract No. HPRN-CT-1999-00164), Deutscher Akademischer Austauschdienst (DAAD), Deutsche Forschungsgemeinschaft (Project No. ZA146/14-1), Grants-in-Aids for Creation Scientific Research (Grant No. 14GS0213), the 21st Century COE establishment Program (Grant No. 14COEB01) from the Ministry of Education, Culture, Science, Sports, and Technology of Japan, and the NEDO International Collaboration "Electrical Doping of π -Conjugated Molecules: Development of New Devices via the Clarification of Mechanisms"; Y.S. acknowledges DAAD for financial support for her stay at Chemnitz. We also acknowledge Professor W. Brütting of Universität Augsburg and Dr. M. Muccini of Istituto per lo Studio dei Materiali Nanostruttu-

rati (ISMN) for information about the facial isomer of Alq_3 , and Professor Furukawa of Waseda University for advice on interpreting the vibrational spectra.

- ¹C. W. Tang and S. Av. Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ²N. Johansson, T. Osada, S. Stafström, W. R. Salaneck, V. Parente, D. A. dos Santos, X. Crispin, and J. L. Bredas, *J. Chem. Phys.* **111**, 2157 (1999).
- ³A. Curioni, M. Boero, and W. Andreoni, *Chem. Phys. Lett.* **294**, 263 (1998).
- ⁴I. Fujii, N. Hirayama, J. Ohtani, and K. Kodama, *Anal. Sci.* **12**, 153 (1996).
- ⁵G. P. Kushto, Y. Iizumi, J. Kido, and Z. H. Kafafi, *J. Phys. Chem. A* **104**, 3670 (2000).
- ⁶M. Cölle, R. E. Dinnebier, and W. Brütting, *Chem. Commun. (Cambridge)* **23**, 2908 (2002).
- ⁷M. Cölle, S. Forero-Lenger, J. Gmeiner, and W. Brütting, *Phys. Chem. Chem. Phys.* **5**, 2958 (2003).
- ⁸M. Muccini, M. A. Loi, K. Kenevey, R. Zamboni, N. Masciocchi, and A. Sironi (private communication).
- ⁹C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **89**, 449 (2001).
- ¹⁰C. Shen, I. G. Hill, A. Kahn, and J. Schwartz, *J. Am. Chem. Soc.* **122**, 5391 (2000).
- ¹¹A. Rajagopal and A. Kahn, *J. Appl. Phys.* **84**, 355 (1998).
- ¹²R. Q. Zang, X. Y. Hou, and S. T. Lee, *Appl. Phys. Lett.* **74**, 1612 (1999).
- ¹³P. He, F. C. K. Au, Y. M. Wang, L. F. Cheng, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.* **76**, 1422 (2000).
- ¹⁴V.-E. Choong, M. G. Mason, C. W. Tang, and Y. Gao, *Appl. Phys. Lett.* **72**, 2689 (1998).
- ¹⁵M. Probst and R. Haight, *Appl. Phys. Lett.* **70**, 1420 (1997).
- ¹⁶M. G. Mason *et al.*, *J. Appl. Phys.* **89**, 2756 (2001).
- ¹⁷A. Curioni and W. Andreoni, *J. Am. Chem. Soc.* **121**, 8216 (1999).
- ¹⁸T. Schwieger, H. Peisert, M. Knupfer, M. S. Golden, and J. Fink, *Phys. Rev. B* **63**, 165104 (2001).
- ¹⁹M. D. Halls and R. Aroca, *Can. J. Chem.* **76**, 1730 (1998).
- ²⁰A. D. Esposti, M. Brinkmann, and G. Ruani, *J. Chem. Phys.* **116**, 798 (2002).
- ²¹T. U. Kampen, G. Salvan, M. Friedrich, D. A. Tenne, S. Park, and D. R. T. Zahn, *Appl. Surf. Sci.* **166**, 387 (2000).
- ²²M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, and A. Sironi, *J. Am. Chem. Soc.* **122**, 5147 (2000).
- ²³G. Salvan, Y. Sakurai, A. Yu. Kobitski, R. Scholz, S. Astilean, T. U. Kampen, D. R. T. Zahn, H. Ishii, and K. Seki, *Appl. Surf. Sci.* **190**, 371 (2002).
- ²⁴T. Yokoyama *et al.* (unpublished).
- ²⁵C. Ganzorig and M. Fujihira, *Appl. Phys. Lett.* **81**, 3137 (2002).