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Infrared Photodissociation Spectroscopy of *n*-Propylbenzene−Ar Cluster Cations: Charge Delocalization between the Aromatic Ring and the Alkyl Chain

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Infrared photodissociation spectra of *n*-propylbenzene−Ar cluster cations have been observed for the CH stretching vibrational region. Because of very small perturbations due to the Ar cluster formation, the spectra of the cluster cations can be practically regarded as those of the corresponding bare cations. The spectra of the cluster cations were compared with infrared spectra of neutral *n*-propylbenzene. It was found that substantially spectral changes take place upon ionization not only for the aromatic CH but also for the alkyl CH stretching vibrations. This fact indicates that the positive charge is not localized in the aromatic ring but is penetrated into the propyl side chains.

I. Introduction

Separability between π electrons of an aromatic ring and electrons of σ bonds in an adjoining alkyl chain is a basic but still unresolved problem in chemistry.[1] When alkylbenzene is ionized to its cationic ground state, a simple consideration of dominant electron configurations indicates that the electron is removed from the aromatic ring. However, the positive charge is known to spread over the whole molecule, partially into the alkyl side chain moiety through the interaction between the π system and the alkyl chain (so-called hyperconjugation). Characterization of such a charge delocalization into the alkyl side chain is very important for examining an efficient charge transfer in biological systems involving aromatic rings.[2]

Recently we measured infrared (IR) spectra of the benzene, toluene, and ethylbenzene cations in the gas phase by using the “messenger” technique.[3] In this technique, van der Waals clusters consisting of molecular cation and Ar atom are prepared, and their IR spectra are measured by monitoring its dissociation yield as a function of the IR excitation frequency.[4] The Ar atom plays a role of the “messenger” of the IR absorption of the molecular cation. Because of negligible perturbations by the cluster formation with Ar, the observed IR spectra can be regarded as those of the bare molecular cations,[3,5] and this technique has been widely applied to observe IR spectra of isolated cations in gas phases.[3−10] In our previous work, it was demonstrated that the CH stretching vibrations of the methyl group in toluene are remarkably changed in both frequencies and intensities upon the ionization, reflecting the charge delocalization.[3] Though hyperconjugation is generally recognized to be less important with an increase of the alkyl chain length, the IR spectrum of the ethylbenzene cation also shows clear evidence of substantial hyperconjugation. Thus, it is an interesting subject to investigate hyperconjugation in alkylbenzene cations with a longer side chain. In this study, we apply the Ar messenger technique in order to observe the CH stretching vibrations of *n*-propylbenzene (*n*-PB) cations. The spectra of the cations are compared with those of the neutral ground state, and effects of the charge delocalization are discussed in combination with theoretical calculations.

II. Experiment

The infrared−ultraviolet (IR−UV) double resonance technique was used for IR spectroscopy of jet-cooled *n*-PB and *n*-PB−Ar in the neutral ground state (S_0), while IR spectra of the *n*-PB−Ar cations in the ground state (D_0) were obtained by using infrared photodissociation (IRPD) spectroscopy, respectively. Both techniques have been described elsewhere in detail.[11] Here we give only a brief description for each method.

(a) IR−UV Double Resonance Spectroscopy in S_0. A pulsed UV laser beam whose wavelength is fixed at the origin band of the S_1−S_0 transition of the compound is introduced, and the ion current signal generated by resonance enhanced multiphoton ionization (REMPI) is monitored as a measure of the ground-state population. Prior to the UV pulse, an IR laser pulse is introduced, and its wavelength is scanned. When the IR wavelength is resonant on a vibrational transition of the compound leading to the IR absorption, the vibrational excitation induces a reduction of the population and is detected as a decrease of the REMPI signal intensity. Thus, the IR spectrum is obtained as the ion current dip spectrum.

(b) IRPD Spectroscopy in D_0. The *n*-PB−Ar cation is produced by two-color photoionization of the neutral cluster for its internal energy to be suppressed. The first UV pulse excites the neutral cluster to the zero point level of S_1, and the second UV pulse ionizes it. The internal energy of the cluster cation is kept below 300 cm^{-1} by using a suitable photon energy of the latter laser. After a delay time of 50 ns, the IR pulse is introduced. When the IR wavelength is resonant on a vibrational transition of the cluster ion, the excitation causes its vibrational predissociation, leading to a depletion of the cluster ion intensity. Thus, by scanning the IR wavelength while monitoring the ion intensity due to the mass-selected cluster ion, the IR spectrum of the cluster ion is obtained as the depletion spectrum.

The sample was heated to 360 K, and its vapor was seeded in Ar gas of 3 atm stagnation pressure. The gaseous mixture was expanded into a vacuum chamber through a pulsed nozzle. Typical background pressure of the chamber is 7×10^{-6} Torr. The jet expansion was skimmed by a skimmer of 2 mm diameter, and the resulting molecular beam was introduced into the interaction region with the laser pulses. A time-of-flight mass

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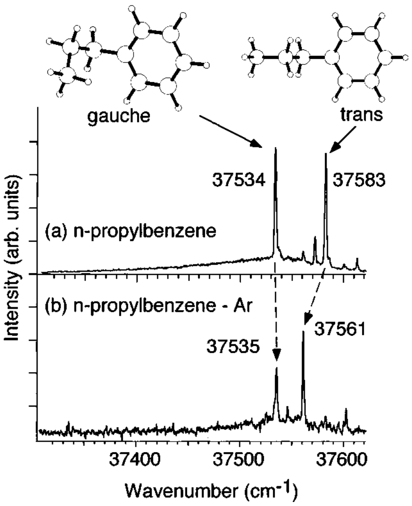


Figure 1. Mass-selected resonance enhanced multiphoton ionization (REMPI) spectra of (a) *n*-propylbenzene and (b) *n*-propylbenzene−Ar in the origin band region of the S_1-S_0 transition. The $m/e = 120$ and $m/e = 160$ ions were monitored, respectively. Two intense bands in each spectrum are the origin bands of the gauche and trans rotational isomers (see text).

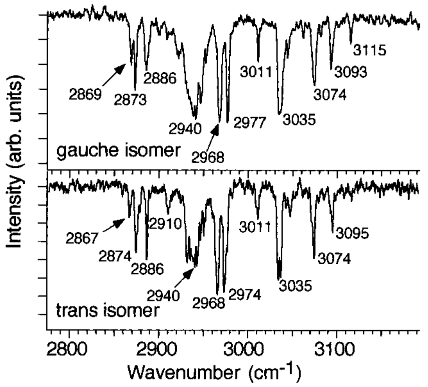
spectrometer of the Wiley−McLaren type was used for the mass-separation of ions.[12]

III. Results and Discussion

(a) S_1-S_0 Spectra of *n*-PB and *n*-PB−Ar. Figure 1 shows the mass-selected REMPI spectra of jet-cooled *n*-PB and *n*-PB−Ar for the origin band region of their S_1-S_0 transitions. The spectrum in Figure 1a is obtained by monitoring the bare molecular cation ($m/e = 120$), exhibiting two bands at 37 534 and 37 583 cm^{-1}. The S_1-S_0 transition of *n*-PB in a supersonic jet expansion was first studied by Hopkins et al., and these two peaks have been assigned to the origin bands of the gauche and trans rotational isomers.[13] The geometrical structures of both the rotational isomers are also illustrated in Figure 1. Because the stabilization due to the self-solvation of the aromatic ring with the propyl chain is expected only for the gauche isomer, Hopkins et al. assigned the lower frequency band (37 534 cm^{-1}) to the gauche isomer and the higher frequency band (37 583 cm^{-1}) to the trans isomer. Takahashi et al. measured zero kinetic energy (ZEKE) photoelectron spectra of the *n*-PB cations via the two S_1 origin bands.[14] The observed ZEKE spectra via the different S_1 origins showed a clear difference in the benzene ring modes as well as in the low-frequency torsional and bending modes, suggesting that the two bands are due to its rotational isomers. Dickinson et al. observed partially resolved rotational structures of the origin bands and analyzed them with the aid of ab initio calculations.[15] As a result, they confirmed the previous assignments given by Hopkins et al. Recently, Fourier transform microwave spectroscopy was applied to *n*-PB in a molecular beam, and coexistence of the trans and gauche isomers has been proven.[16]

The spectrum in Figure 1b is obtained by monitoring the *n*-PB−Ar cation ($m/e = 160$), showing two intense bands at 37 535 and 37 561 cm^{-1}. Upon the cluster formation of an aromatic compound with Ar, a low-frequency shift is generally expected for the S_1-S_0 origin.[17] Therefore, the band at 37 561 cm^{-1} is reasonably assigned to the origin band of the trans isomer of *n*-PB−Ar. The low-frequency shift of 22 cm^{-1} is typical for such cluster formation. The origin band of the gauche isomer of *n*-PB−Ar is expected to have nearly the same intensity as that of the trans isomer, because the abundance of the isomers of bare *n*-PB is nearly the same in the jet expansion, as seen in the intensity ratio of the origin bands in spectrum a. Therefore, the band at 37 535 cm^{-1} should be assigned to the origin band of the gauche isomer of *n*-PB−Ar, though it exhibits an extremely small shift (+1 cm^{-1}) of the electronic transition, which is unusual for the cluster formation with Ar. This assignment is confirmed by the results of the IR−UV double resonance spectroscopy given in the next section, and the origin of the unusual shift will also be discussed.

(a) n-propylbenzene IR-UV spectra



(b) n-propylbenzene simulated IR spectra

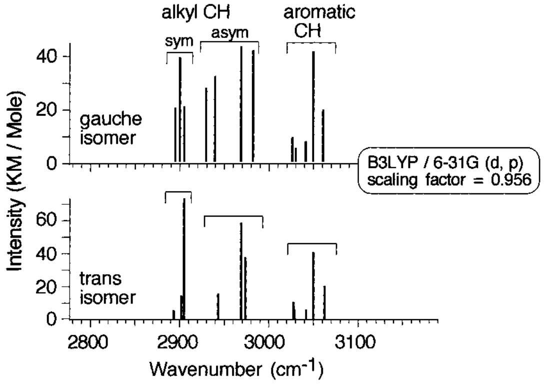
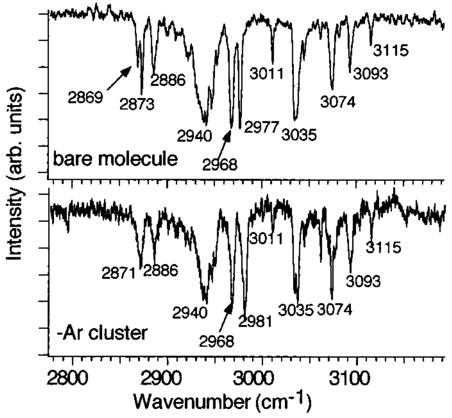


Figure 2. (a) CH stretching vibrational region of the infrared−ultraviolet (IR−UV) spectra of the (upper) gauche and (lower) trans isomers of *n*-propylbenzene in the neutral electronic ground state (S_0). (b) Simulated IR spectra of the (upper) gauche and (lower) trans isomers of *n*-propylbenzene in S_0. The simulation is based on the B3LYP/6-31G(d,p) level calculations. The scaling factor of 0.954 is applied to the calculated vibrational frequencies to fit with the observed spectra (see text).

(b) IR Spectra of *n*-PB and *n*-PB−Ar in S_0. Figure 2a shows the IR spectra for the CH stretching region of the gauche and trans isomers of bare *n*-PB in S_0. In each spectrum, the REMPI signal via the origin band of the S_1-S_0 transition was monitored, and the depletion of the REMPI intensity due to the IR absorption was recorded as a function of the IR wavelength. Since the characteristic vibrational frequencies of alkyl and aromatic CH stretching vibrations are well-known, the bands seen in the 2850−3000 cm^{-1} range are attributed to the CH stretches of the propyl chain, and those above 3000 cm^{-1} are due to the aromatic CH stretches.[18] The IR spectra of the isomers are quite similar to each other not only in the aromatic CH region but also in the alkyl CH region. Despite the large conformational difference of the propyl chain, most of the corresponding bands have nearly the same vibrational frequencies (within 3 cm^{-1}), and the intensity distributions are also quite similar.

Figure 2b shows the simulated IR spectra of the gauche and trans isomers of neutral *n*-PB. The simulation is based on the


(a) IR-UV spectra of the gauche isomer in S_0

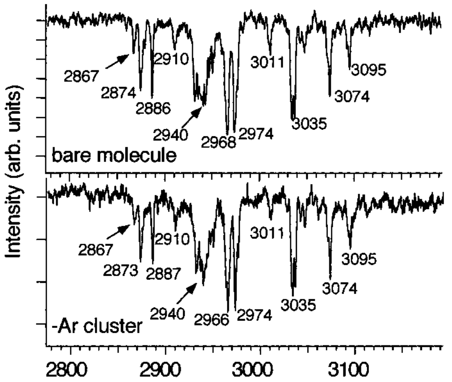
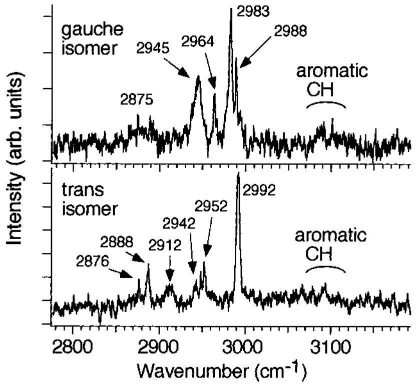

(b) IR-UV spectra of the trans isomer in S_0

Figure 3. Comparison between the IR−UV spectra of *n*-propylbenzene and its Ar clusters in S_0: (a) gauche isomer; (b) trans isomer. The upper traces in (a) and (b) are the IR−UV spectra of bare *n*-propylbenzene. The lower traces of (a) and (b) are those of the *n*-propylbenzene−Ar clusters.


(a) (n-propylbenzene-Ar)+IRPD spectra

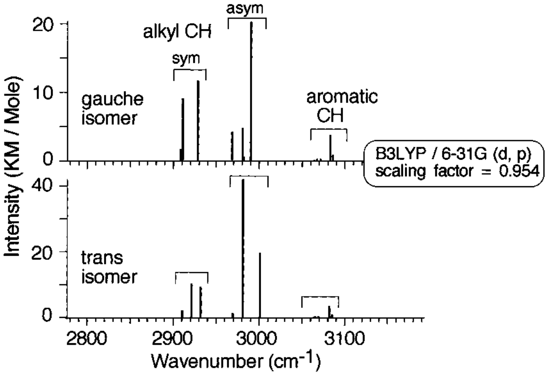

(b) n-propylbenzene+ simulated IR spectra

Figure 4. (a) Infrared photodissociation (IRPD) spectra of the (upper) gauche and (lower) trans isomers of the *n*-propylbenzene−Ar cluster cations in the CH stretching vibrational region. (b) Simulated IR spectra of the (upper) gauche and (lower) trans isomers of *n*-propylbenzene cations. The simulation is based on the B3LYP/6-31G(d,p) calculations. The scaling factor of 0.954 is applied to the calculated vibrational frequencies to fit with the observed spectra.

energy-optimized structures with the density functional theoretical (DFT) calculations at the B3LYP/6-31G(d,p) level,[19] using the Gaussian 98 program package.[20] The harmonic approximation was involved in evaluating the vibrational frequencies, and a scaling factor of 0.956 was applied to fit them to the observed. The simulated spectra qualitatively reproduce the observed spectra. The overall spectral ranges of the alkyl and aromatic CH stretches and intensity ratio between these two types of the CH stretches are well reproduced, while the simulation of band positions and intensities is rather poor. It is noticed that the number of the observed CH bands (including shoulders) is more than those expected (7 for the alkyl CH and 5 for the aromatic CH). This indicates that extensive Fermi resonance of the CH modes with overtones and/or combinations makes the spectra complicated.

As is intuitively expected, the simulated spectra show remarkable differences in both intensities and band positions of the alkyl CH stretches between the gauche and trans isomers, while nearly the same spectra were predicted for the aromatic CH stretches. In the observed spectra, however, both the isomers show quite similar spectral features even in the alkyl CH stretch region. The simulation clearly overestimates the conformation dependence of the alkyl CH vibrations. We also found the similar tendency in the Hartree−Fock self-consistent field (HF/SCF) calculations.

IR spectra of gauche and trans *n*-PB−Ar are given in the lower traces of Figure 3a,b, respectively. For comparison, corresponding spectra of the bare *n*-PB isomers are also shown in the upper traces. The IR spectra of the Ar clusters are quite similar to those of the corresponding bare isomers. Even minor differences between the bare isomers, i.e., the band shape of the broad band at 2940 cm^{-1} and the intensity of the band at 3115 cm^{-1}, are well reproduced in the spectra of the clusters. In this respect, the good correspondence of the spectra between the bare and cluster isomers indicates that the assignments of the cluster bands in the electronic spectra are unambiguous.

Although no structure of the *n*-PB−Ar clusters has been reported, the fact that the aromatic CH stretches exhibit no shift upon the cluster formation strongly suggests that the Ar atom is located on the aromatic ring. In the case of the trans isomer cluster, the low-frequency shift of 22 cm^{-1} in the S_1-S_0 origin band is consistent with such cluster structure.[17] On the other hand, the extremely small shift in the gauche isomer (+1 cm^{-1}) seems to be quite unusual, if we simply assume the ordinary aromatic−Ar interactions. A possible explanation for this unusual shift is that the Ar atom resides on the same side of the ring as the propyl chain, and it is solvated not only by the aromatic ring but also by the propyl group. Upon the electronic excitation to the S_1 state, the stabilization energy between the Ar atom and aromatic ring may be canceled by the repulsive interaction between the Ar atom and propyl chain leading to the almost zero shift of the origin band.

(c) IR Spectra of the *n*-PB−Ar Cations in D_0. Figure 4a shows IRPD spectra of the gauche and trans *n*-PB−Ar cluster cations in the CH stretching vibrational region. In these spectra, the depletion of the cluster ion intensity (m/e = 160) due to vibrational predissociation was measured as a function of the IR wavelength. As seen in the IR spectra of the clusters in S_0, the perturbation due to the cluster formation with Ar is expected to be very small for the CH stretching vibrations. Thus, the observed spectra of the cluster cations can be practically regarded as those of the bare cations.

The IR spectra of the *n*-PB−Ar cations are totally different from those of the corresponding neutral clusters with respect to the number of bands and to the band positions. The aromatic CH bands become quite weak upon the ionization, and only traces of the bands are seen around 3090 cm^{-1}. The alkyl CH stretches also show significant changes. A few strong bands are seen in the 2900−3000 cm^{-1} range, and they are assigned to the asymmetric CH stretches of the propyl chain based on DFT calculations described below. Much weaker bands appear in the region where the symmetric CH stretches of the alkyl chain are expected.

The simulated IR spectra of the gauche and trans *n*-PB cations are shown in Figure 4b. The simulation is performed by the same level of theory as that used for the neutrals. The simulation reproduces qualitatively the observed IR spectra. The IR intensities of the aromatic CH stretches drastically decrease upon the ionization, and slight high-frequency shifts are predicted, in accordance with the observed spectra. The same tendencies have already been found for ionization of other alkylbenzenes, such as toluene and ethylbenzene.[3] The simulation also predicts the stronger intensities of the asymmetric alkyl CH stretches than those of the symmetric alkyl CH stretches. The details of the alkyl CH stretches are poorly simulated by the DFT calculations. As seen in the spectra of the neutral ground state, Fermi mixing might be responsible for the discrepancy between the observed and calculated spectra.

(d) Charge Delocalization in the *n*-PB Cations. The ionization of *n*-PB to its cationic ground state is usually interpreted by π electron ejection from the aromatic ring under a crude approximation. If the produced positive charge is really localized in the aromatic ring, the vibrational spectra of the propyl moiety should show only a minor change upon the ionization. However, the observed IR spectra of the cations are significantly changed even for the alkyl CH stretches. This fact clearly demonstrates that the positive charge is not localized in the aromatic ring but is penetrated into the propyl side chains.

Drastic changes of alkyl CH stretching vibrations upon ionization have been also found for toluene and ethylbenzene.[3] Especially in the case of ethylbenzene, the IR spectrum of its cation exhibits the same characteristics of the *n*-PB cations, such as strong asymmetric alkyl CH, weak symmetric alkyl CH, and substantial reduction of the aromatic CH stretch intensity. Despite the increase in the alkyl chain length, the spectral changes upon the ionization of *n*-PB seem to be similar to those in ethylbenzene.

To estimate the extent of the charge delocalization, we performed natural bond orbital (NBO) charge population analysis.[21] On the basis of the energy-optimized structures used to simulate the IR spectra, we calculated NBO charge in the B3LYP/6-31G(d,p) level. No difference is found between the rotational isomers with respect to the charge delocalization in both S_0 and D_0. Because of the weak electron donating property of the propyl group, the propyl group is positively charged even in S_0. However, the net charge in the propyl group is very small (only 0.03 AU), and both the aromatic and propyl groups are essentially neutral. In the D_0 state, the NBO analysis predicts that 17% of the positive charge is distributed to the propyl chain and 83% to the aromatic ring. This result supports the charge delocalization effect indicated by the observed IR spectra.

We also performed the NBO charge population analysis at the same level of the calculation for toluene and ethylbenzene in S_0 and D_0. In the S_0 state, the methyl and ethyl groups have very small positive charge (0.03 AU in both the groups). The net charge of the methyl and ethyl group in the D_0 state is 16 and 18% of the total positive charge, respectively. These results are quite similar to those of *n*-PB, and nearly the same extent of the charge delocalization to the alkyl chain is predicted among these cations, despite the different chain lengths. These estimations are well consistent with the fact that the ethylbenzene and *n*-PB cations exhibit quite similar characteristics with respect to the alkyl CH stretch region.[3] It should, however, be noted that the above discussion based on the DFT calculations may be still qualitative because the IR spectra based on the DFT calculations only qualitatively reproduce the observed spectra.

Finally, it is worthwhile to note that the IR spectra in the cationic ground state show a remarkable isomer dependence in the alkyl CH region of the *n*-PB cations, though the IR spectra in the neutral S_0 state are quite similar between both rotational isomers. In electronic spectroscopic studies, a similar tendency has been found; the vibronic structures in the S_1−S_0 electronic spectra of the gauche and trans isomers are nearly the same except for the shift of the origin band positions, while the ZEKE spectra of the isomers via their S_1 origins show quite different low-frequency bands.[14] Since the Franck−Condon active modes in the ZEKE spectra are associated with large geometric changes between the neutral and cationic states, such an isomer dependence of the low-frequency modes indicates that the conformational change of the propyl chain should be involved upon the ionization. If the positive charge is distributed in both the aromatic ring and the propyl chain, it is reasonable to expect that stronger interactions through space between the propyl chain and the aromatic ring than those in the neutrals, resulting in the stronger isomer dependence of the IR spectra. Thus, the isomer dependence of the *n*-PB cations would be regarded as another indication of the charge delocalization into the alkyl chain. There are also alternative explanations for the isomer dependence; in the case of the gauche isomer, the Ar solvation possibly gives small perturbation to the propyl group, though there is no sign of such perturbation in S_0. The enhanced polarization interaction between the charge on the ring and propyl group also could contribute to the isomer dependence in the cation. Whatever the origin of the isomer dependence, both the isomer cations showed the remarkable changes in the alkyl CH stretches upon ionization. This fact indicates that the charge delocalization effect is almost common between the isomer cations.

IV. Concluding Remarks

In this study, we applied the Ar messenger technique in order to observe the IR spectra of the *n*-PB cations in the CH stretching vibrational region. The observed spectra of the cations showed remarkable differences from those of the neutrals in respect to not only the aromatic CH stretches but also the alkyl CH stretches. This result indicates that the positive charge of the cations is delocalized into the alkyl chain. The NBO analysis based on the DFT calculations was performed, and nearly the same extent of the charge delocalization to the alkyl chain is predicted among the toluene, ethylbenzene, and *n*-PB cations, despite the different chain lengths. Though the estimation should be regarded as qualitative, it is consistent with the significant changes of the alkyl CH stretching vibrations in these molecules upon the ionization.

Charge distribution is the most essential information to consider problems concerning charge delocalization. Though the development of theoretical calculation techniques and resources enables us to estimate it easily, calculated results still cannot be regarded to be very accurate because of some theoretical and conceptual problems.[22] Moreover, no direct experimental verification of the charge distribution is practically available at the present stage. Therefore, it is very important to develop experimental techniques to extract any information on the charge delocalization. Some of molecular vibrations are localized on a functional group, and observation of such characteristic vibrations gives us detailed information on changes of electronic structures upon ionization. In addition, IR spectroscopy provides experimental examinations for the improvement of theoretical calculations because observed IR spectra can be directly compared with theoretical calculations.

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