



Infrared gas phase absorption spectra of neutral and cationic toluene–argon complexes

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Abstract

The infrared absorption spectrum of both neutral and cationic toluene–argon has been measured in the range from 400 to 1700 cm^{-1} . The spectrum of the neutral complex compares well to previously measured spectra of toluene, whereas the spectrum of the cationic species represents the first complete survey of the vibrational structure of the cation. Both spectra are compared to results from ab initio calculations.

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1. Introduction

Already around the turn of the twentieth century, the vibrational structure of toluene and many other organic molecules was recorded. The first spectra which revealed this vibrational structure were infrared spectra obtained by 1904 [1]. With the advent of laser spectroscopy, much more was learned about the spectroscopy of the toluene molecule as well as of various complexes consisting of toluene and some small adduct. The vibrational structure of the neutral toluene molecule has been studied extensively by several methods: in the liquid phase by absorption through a cell [1], in a gas cell [2,3], and by recording the fluorescence

from the first excited singlet state (S_1) [4,5]. The IR spectrum of toluene is found to be similar to that of benzene, with additional features arising from the attachment of the methyl group [2–6]. Due to this close resemblance with benzene, the ‘Wilson’ mode assignment convention is often adopted, which is quite different from usual spectroscopic conventions [5,7,8].

In a comprehensive study on the ground and first electronically excited state of toluene, Borst and Pratt [9] measured rotationally resolved spectra. From these experiments it is concluded that the methyl group is oriented such that all hydrogens are out of plane with respect to the aromatic ring (staggered) in both the electronic ground state and the excited state. In the cation, the molecule geometry is changed with respect to the neutral state by a rotation of the methyl group such that one hydrogen is now in plane with

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respect to the aromatic ring (eclipsed). In the ground electronic state, the barrier for methyl rotation is known to be low [9], and as a consequence the orientation of the methyl group should not necessarily be viewed as fixed.

In the case of benzene, due to the presence of the Jahn–Teller instability, the vibrational structure of the cation is of considerable interest and its IR spectrum has been shown to be complicated [10]. In the toluene cation, no such geometry distortion is expected. There are, however, other reasons to investigate its vibrational structure. The toluene cation is one of the most studied species in gas phase ion chemistry, as $C_7H_7^+$ can be formed from it with relative ease and the conversion between isomeric structures of this species is especially interesting. In particular, the isomerization to form the seven membered ring ‘tropylium’ ion has been intensely studied and many open questions remain [11].

Little information is available on the vibrational structure of the toluene cation, as most studies on the toluene cation are focussed on the internal rotation of the methyl group with respect to the aromatic ring [12,13]. For cationic toluene–argon complexes, the intermolecular vibrations of the argon atom with respect to toluene have received most attention [14,15]. However, some information was obtained using photo-electron spectroscopy [16,17]. Direct infrared absorption spectra in the C–H stretch spectral region have also been obtained [18].

Mid- and far-infrared spectra of cold gas phase molecules and molecular ions can be obtained by using dissociation of weakly bound molecular complexes [19] in combination with a tunable infrared (IR) source [20–23]. In this technique, molecule–noble gas complexes are irradiated with infrared light. When the radiation is resonant with an IR active mode of the complex, and the photon energy is above the dissociation limit of the complex, then the complex can dissociate. Monitoring the dissociation yield as a function of IR wavelength, makes it possible to record the IR spectrum of the complex. This spectrum of the complex is not necessarily identical to the spectrum of the bare molecule. However, discrepancies are generally found to be small [10,20,22].

The weakly bound complex which is used in this experiment is the toluene–argon complex. The structure of the toluene–argon complex has been studied in less detail than the bare molecule. Since a rotationally resolved spectrum of the toluene–argon complex has not been recorded yet, it is a priori not known where the argon atom is located with respect to the toluene molecule. However, observations of the van der Waals vibrations of the argon atom with respect to the toluene molecule indicate that its most probable location is above the aromatic ring [14,24].

2. Experiment

The experimental setup has been described elsewhere [25] and only a brief description is given here. A mixture of toluene, at a partial pressure of about 40 mbar (vapor pressure at 25 °C), in 3 bar of argon is injected into the vacuum chamber by means of a pulsed valve. This mixture expands into vacuum and forms complexes. The molecular beam is crossed by the IR beam of free electron laser for infrared experiments (FELIX) [26,27] and the beam of an UV laser.

When measuring the IR spectrum of the neutral complex, we first irradiate the molecular beam with the FEL macropulse after which the beam is probed for neutral toluene–argon complexes using resonance enhanced multi-photon ionization (REMPI). The wavelength of the UV laser is resonant with the transition from the vibrationless electronic ground state to the vibrationless first excited state ($S_1 \leftarrow S_0$) of the toluene–argon complex, at $37\,450\text{ cm}^{-1}$ [9]. A second photon from the same source will ionize the complex with about 3900 cm^{-1} of excess energy with respect to the ionization potential (IP) [12]. Time-of-flight mass spectra are recorded and the ion current on the mass channel $m/z = 132$ is monitored. In Fig. 1, a schematic energy level diagram is shown. When FELIX is resonant with a vibration that is above the dissociation limit of the complex, which is on the order of 300 cm^{-1} [20,23,28], the complex will dissociate and a decrease will be seen in the ion signal in the mass spectrum.

A slightly different scheme is used when performing experiments on cationic complexes.

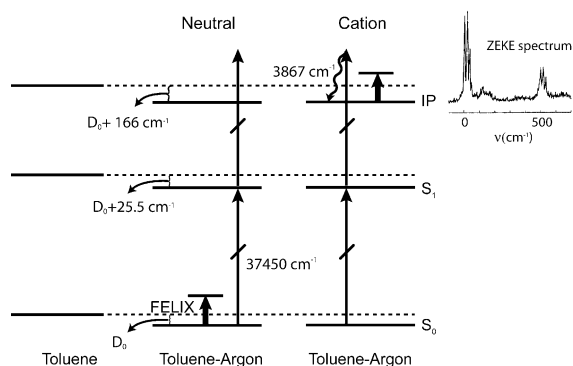


Fig. 1. The energy level scheme relevant for the experiments. In the experiments on the neutral species, FELIX irradiates the complex first, after which the amount of ground state complexes is probed by two photon ionization. In the experiments on the cationic species, complexes are first ionized, after which they are irradiated with FELIX. Also shown is the ZEKE spectrum as obtained by Kimura and co-workers [14].

Cationic complexes are produced in a field-free environment using the same 1 + 1 REMPI scheme. Since the ionizing photon brings the complex to an energy of 3900 cm^{-1} above the IP, a certain fraction of the complexes will dissociate to form bare toluene ions. However, about 25% of the excited complexes end up in states that do not dissociate, all of which are expected to be below or just barely above the dissociation limit of the cationic ground state. The relative population of the various levels depends on their Franck–Condon overlap with the S_1 state, which is known from zero electron kinetic energy (ZEKE) spectroscopy. Shown in Fig. 1 is a plot of a ZEKE spectrum of the toluene–argon complex taken by Kimura and co-workers [14]. The relative intensities in the ZEKE spectrum correspond to the population probability when excess energy is used in the ionization process. It is seen from this ZEKE spectrum that, apart from ions in the vibrationless level, ions with a few van der Waals modes excited will also be produced. In addition, there might be some population in the modes observed around 500 cm^{-1} .

Once ionized, the complexes are irradiated with FELIX, and upon making a vibrational transition to a level above the dissociation limit, they will dissociate. One microsecond after the end of the FEL macropulse, high voltage is applied to the

extraction electrodes, and the ions are accelerated toward the detector.

3. Results

3.1. The neutral toluene–argon complex

By employing the ion-dip technique described in Section 2, we have recorded the infrared spectrum of the neutral toluene–argon complex in the electronic ground state. The spectrum is shown in Fig. 2. Two resonances near 700 cm^{-1} dominate the spectrum. Of these modes, the mode at 727 cm^{-1} corresponds to the ν_{11} ‘umbrella’ mode, also found to be strong in the IR spectrum of benzene. In order to gain a better understanding of the toluene–argon infrared spectrum, we calculated the vibrational frequencies and infrared transition intensities for bare toluene, using quantum chemical methods available in the GAUSSIAN 98 package [29]. For neutral and ionic aromatic molecules, the B3LYP method with the D95(d,p) basis set has been shown to yield reliable vibrational frequencies and IR intensities [30,31]. The optimized geometry has C_s symmetry. In the lower trace of Fig. 2 the calculated spectrum is shown. Also shown is

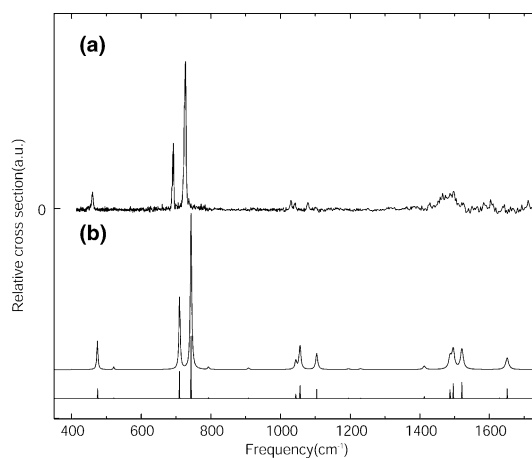


Fig. 2. The infrared spectrum of the neutral toluene–argon complex (a) shown in conjunction with the calculated IR spectrum, shown as a stick spectrum (b), for the bare toluene molecule. Also shown is a convolution of the stick spectrum with a lineshape corresponding to the bandwidth of FELIX.

Table 1
Observed line positions of the vibrations of the toluene–argon complex

$\tilde{\nu}_{\text{obs}}$ (cm^{-1})	$\tilde{\nu}_{\text{calc}}$ (cm^{-1})	Lawrance and co-workers [5]	Mode no. (Char.)	Motion
460	475	464	21 (A')	C–C out of plane bend
692	710	695	19 (A')	C–H out of plane bend
727	744	728	18 (A')	C–H out of plane bend
1033	1044	1030	13 (A')	C–H in plane bend
1043	1056	1040	12 (A')	Methyl bend
1077	1104	1080	32 (A'')	C–H in plane bend
*	1487	1445	8 (A')	Methyl bend
*	1497	1463	27 (A'')	Methyl bend
*	1521	1494	7 (A')	C–H in plane bend

Also listed are calculated frequencies from a quantum chemical calculation at the B3LYP/D95(d,p) level, frequencies such as observed by Lawrance and co-workers [5], number and character of the calculated mode and atomic motion. Modes that are part of the broad and unresolved feature near 1500 cm^{-1} are indicated with an asterisk.

a convolution of this stick spectrum with a lineshape-function corresponding to the bandwidth of the laser, including the linear increase in width with increasing frequencies. All features in the experimental spectrum are found back in the calculated spectrum, and good agreement, both in line position and in line intensity, is found.

All experimentally observed lines can be unambiguously assigned except for the feature near 1500 cm^{-1} which is unresolved and most likely consists of several modes, in agreement with the calculations. In Table 1 the observed vibrational frequencies are listed, together with the calculated values and the values recently compiled and measured by Lawrance and co-workers [5]. For the current experiments, we estimate the accuracy in line position to be about 0.5% of the central wavelength. The accuracy in the vertical scale is estimated to be 10% of the observed cross-section. Taking this into account we can conclude that the values presented here are in good agreement with previous experiments [1–5]. The normal modes from the calculations can be visualized and assigned. The resulting assignments following the Mulliken notation [8] as well as in terms of the atomic motion are also given in the table.

3.2. The cationic toluene–argon complex

When the toluene–argon complexes are first ionized and the resulting complex ions are then irradiated by the IR beam, the IR absorption

spectrum of the ionic complex can be measured. The spectrum is shown in Fig. 3 together with a stick spectrum that is extracted from ab initio calculations on the toluene cation. Calculations on the toluene cation are performed at the same level as the neutral ground state with the main difference being a change in geometry upon ionization; compared to the ground state, the methyl group is rotated by 30° . Also shown is a convolution of this stick spectrum with a 15 cm^{-1} full-width half maximum (FWHM) Lorentzian lineshape-func-

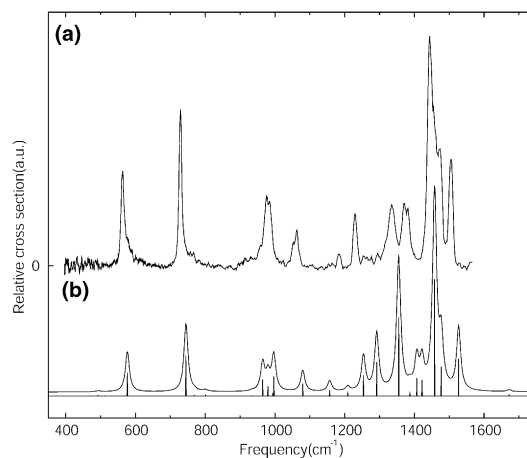


Fig. 3. The infrared spectrum of cationic toluene–argon (a) together with the calculated IR spectrum, shown as a stick spectrum, of the bare toluene cation (b). This stick spectrum is also convoluted with a lineshape that has a fixed width of 15 cm^{-1} FWHM.

tion. All lines in the experimental spectrum are observed to be significantly broader. This additional broadening might arise from the ensemble of states that is prepared during ionization.

The positions and relative intensities of the two lines at low frequencies, at 564 and 729 cm^{-1} , are in good agreement with the predictions of the calculations. Some asymmetry is observed in these line shapes. Closer to 1000 cm^{-1} , the abundance of modes both in the experimental and theoretical spectrum makes an assignment harder. The peak observed around 970 cm^{-1} , clearly has substructure and consists of at least three unresolved peaks at 959, 976 and 985 cm^{-1} . This is also consistent with the results from the calculations. There are four fundamental modes found in this range (at 965, 980, 995 and 997 cm^{-1}). The mode at 995 cm^{-1} is calculated to be very weak and only 2 cm^{-1} away from a neighbouring mode, so that we would not expect to observe that mode in the experiment. We therefore assign these three modes to the three strong modes which are predicted in this region. Further up the energy scale, around 1060 cm^{-1} , a feature is observed where the calculations also predict one mode. The next two resonances are observed at 1184 and 1230 cm^{-1} , which are assigned to modes calculated at 1254 and 1292 cm^{-1} . The discrepancy with the calculations is somewhat

larger for these modes than for other modes. Closer inspection reveals that the motions involve predominantly the C–C bond between the methyl group and the aromatic ring, both the stretching and the in-plane bending of this bond. Apparently, this part of the potential energy surface is not described sufficiently accurately, resulting in the larger difference between the calculated and observed positions for these modes. In the region between 1300 and 1400 cm^{-1} , two features are observed, one at 1335 cm^{-1} and one feature near 1375 cm^{-1} . The latter seems to consist of two resonances at 1370 and 1381 cm^{-1} . The single feature at 1335 cm^{-1} is assigned to a mode calculated at 1355 cm^{-1} and the two peaks are assigned to modes at 1407 and 1423 cm^{-1} . The last two features in the spectrum are at around 1450 and 1503 cm^{-1} . The feature at around 1450 cm^{-1} has some substructure, arising from two vibrational modes calculated to be at 1458 and 1477 cm^{-1} . The positions of the deconvoluted experimental peaks are 1438 and 1470 cm^{-1} . The feature at 1503 cm^{-1} is assigned to a mode calculated at 1527 cm^{-1} . The observed line positions and calculated values for each of these modes is given in Table 2.

The experimentally observed dip-spectrum can only be converted to a linear absorption spectrum

Table 2
Observed line positions of the vibrations of the toluene–argon cation

$\tilde{\nu}_{\text{obs}}$ (cm^{-1})	$\tilde{\nu}_{\text{calc}}$ (cm^{-1})	Previous observations	Mode no. (Char.)	Motion
564	577	540 ^b	35 (A'')	C–H out of plane bend
729	745		34 (A'')	C–H out of plane bend
959	965		22 (A')	Methyl bend
976	980	978 ^a , 932 ^c	21 (A')	C–C in plane bend
985	997	986 ^a	31 (A'')	C–H out of plane bend
1063	1081	1057 ^b	19 (A')	C–H in plane bend
1184	1254		16 (A')	C–C stretch
1230	1292		15 (A')	C–C in plane bend
1335	1355		14 (A')	Methyl bend
1370	1407		12 (A')	C–C in plane bend
1381	1423	1376 ^b	28 (A')	Methyl bend
1438	1458		11 (A')	C–H in plane bend
1470	1477		10 (A')	Methyl bend
1503	1527		9 (A')	C–H in plane bend

Calculated frequencies (B3LYP/D95(d,p)) are listed together with observations of Inoue et al. (a) [14], Eisenhardt et al. (b) [16], and Meek et al. (c) [17]. Also listed are mode number and character, along with the atomic motion of the mode.

when the dissociation is induced by a single photon. For the benzene–argon complex ion, the dissociation energy is measured to be below 485 cm^{-1} [23] and this can serve as an estimate for the dissociation energy of the toluene–argon complex ion. It is thus clear that in the high frequency region of the spectrum, one photon is sufficient to dissociate the complex. For the lowest frequency peak at 564 cm^{-1} , the situation is not so clear. We therefore measured the dependence of the dissociation yield on laser fluence for this mode. It is observed that the dependence is as expected for a single photon process and it is concluded that the dissociation limit for cationic toluene–argon is below 564 cm^{-1} . Taking the shift in IP between toluene and toluene–argon of 166 cm^{-1} into account [12], we can conclude that the dissociation limit of neutral toluene–argon lies below 398 cm^{-1} .

When comparing the spectrum of the cationic complex to that of the neutral complex, a striking observation is that all lines in the spectrum of the cationic complex are much broader than in its neutral counterpart. This width of the resonances results from the ionization method that is being used. The energy of the ionizing photon is about 3900 cm^{-1} above the IP. This energy will end up in kinetic energy of the electron and/or internal energy of the complex. The distribution of internal vibrational energies is directly linked with the amount of Frank–Condon overlap of this state with the state from which ionization took place. In a ZEKE-spectrum one can observe directly this relative overlap. When then looking at a ZEKE-spectrum taken by Kimura and co-workers [14] (see Fig. 1), one can observe that most of the ions will end up with a vibrationally cold toluene core, but with excited van der Waals vibrations. However, some ions will also have an initial excitation in the toluene core of around 500 cm^{-1} . When the excitation is above the complex binding energy, the complex will most likely dissociate on a short time scale and not contribute to the spectrum measured here [25]. At the moment, the value of the dissociation energy is not well known and only an upper limit of 564 cm^{-1} can be given here. It is concluded therefore, that in the IR spectrum shown here, contributions from vibrationally ex-

cited complexes are present which explain the observed broadening in the spectrum.

There are a few recent publications that deal with the vibrational structure of the toluene cation. There is a ZEKE study of toluene–argon by Kimura and coworkers [14], and two photo-electron (PE) studies, one by Eisenhardt and Baumgärtel [16] and another by Meek et al. [17]. In the ZEKE spectrum, there are three vibrational features that are identified: modes 6b, 12 and 18, which are respectively situated at 484 , 978 and 986 cm^{-1} . The ν_{12} -mode is also observed in the PE-spectrum of toluene [17] at a value of 932 cm^{-1} . In the spectra taken by Baumgärtel et al. several features can be found that might coincide with modes observed here. Specifically the bands observed at 540 (identified as mode 6b), 1057 and 1376 cm^{-1} in the photo-electron spectrum are near to features that we observe. Since photo-electron spectroscopy has no strict selection rules and a generally lower accuracy, a detailed comparison, especially in the high energy region, is difficult.

4. Conclusion

In this Letter both the IR spectrum of neutral toluene–argon as well as cationic toluene–argon is reported in the range between 400 and 1700 cm^{-1} . Although the positions of the vibrational levels are well-known for the neutral toluene molecule, the spectrum presented here provides the first infrared absorption spectrum of the free molecule. The spectrum of the toluene–argon cation represents one of the first complete surveys of the vibrational structure of cationic toluene. Both spectra are in agreement with previous studies on the respective species and with the ab initio calculations reported here.

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References

- [1] W.W. Coblenz, *Astrophys. J.* 20 (1904) 207.
- [2] J.K. Wilmhurst, H.J. Bernstein, *Can. J. Chem.* 35 (1957) 911.
- [3] N. Fuson, C. Garrigou-Lagrange, M.L. Josien, *Spectrochim. Acta* 16 (1960) 106.
- [4] J.I. Selco, P.G. Carrick, *J. Mol. Spectrosc.* 137 (1989) 13.
- [5] C.G. Hickman, J.R. Gascooke, W.D. Lawrance, *J. Chem. Phys.* 104 (1996) 4887.
- [6] K.S. Pitzer, D.W. Scott, *J. Am. Chem. Soc.* 65 (1943) 803.
- [7] E.B. Wilson, *Phys. Rev.* 45 (1934) 706.
- [8] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1997.
- [9] D.R. Borst, D.W. Pratt, *J. Chem. Phys.* 113 (2000) 3658.
- [10] J.M. Bakker, R.G. Satink, G. von Helden, G. Meijer, *Phys. Chem. Chem. Phys.* 4 (2002) 23.
- [11] C. Lifshitz, *Acc. Chem. Res.* 27 (1994) 138.
- [12] K.-T. Lu, G.C. Eiden, J.C. Weisshaar, *J. Phys. Chem.* 96 (1992) 9742.
- [13] W.D. Geppert, C.E.H. Dessent, M.C.R. Cockett, K. Müller-Dethlefs, *Chem. Phys. Lett.* 303 (1999) 194.
- [14] H. Inoue, S. Sato, K. Kimura, *J. Electron Spectrosc. Rel. Phen.* 88–91 (1998) 125.
- [15] S. Sato, T. Kojima, K. Byodo, H. Shinohara, S. Yanagihara, K. Kimura, *J. Electron Spectrosc. Rel. Phen.* 112 (2000) 247.
- [16] C.G. Eisenhardt, H. Baumgärtel, *Ber. Bunsenges. Phys. Chem.* 102 (1998) 1803.
- [17] J.T. Meek, S.R. Long, J.P. Reilly, *J. Phys. Chem.* 86 (1982) 2809.
- [18] A. Fujii, E. Fujimaki, T. Ebata, N. Mikami, *J. Chem. Phys.* 112 (2000) 6275.
- [19] M. Okurnura, L.I. Yeh, J.D. Myers, Y.T. Lee, *J. Chem. Phys.* 85 (1986) 2328.
- [20] J.A. Piest, G. von Helden, G. Meijer, *J. Chem. Phys.* 110 (1999) 2010.
- [21] J.A. Piest, G. von Helden, G. Meijer, *Astrophys. J.* 520 (1999) L75.
- [22] J.A. Piest, J. Oomens, J.M. Bakker, G. von Helden, G. Meijer, *Spectrochim. Acta A* 57 (2001) 717.
- [23] R.G. Satink, J.A. Piest, G. von Helden, G. Meijer, *J. Chem. Phys.* 111 (1999) 10750.
- [24] M. Mons, J. Le Calvé, F. Piuze, I. Dimicoli, *J. Chem. Phys.* 92 (1990) 2155.
- [25] R.G. Satink, J.M. Bakker, G. Meijer, G. von Helden, *Chem. Phys. Lett.* 359 (2002) 163.
- [26] D. Oepts, A.F.G. van der Meer, P.W. van Amersfoort, *Infrared Phys. Technol.* 36 (1995) 297.
- [27] G.M.H. Knippels, R.F.X.A.M. Mols, A.F.G. van der Meer, D. Oepts, P.W. van Amersfoort, *Phys. Rev. Lett.* 75 (1995) 1755.
- [28] D. Cappelletti, M. Bartolomei, F. Pirani, V. Aquilanti, *J. Phys. Chem. A* 106 (2002) 10764.
- [29] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.7, Gaussian, Inc, Pittsburgh, PA, 1998.
- [30] J. Oomens, G. Meijer, G. von Helden, *J. Phys. Chem. A* 105 (2001) 8302.
- [31] C.W. Bauschlicher, E.L.O. Bakes, *Chem. Phys.* 262 (2000) 285.