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Electronic absorption spectra of cold organic cations: 2,4-Hexadiyne

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Abstract

The results of a study with an approach to measure electronic spectra of organic cations whereby both the rotational and vibrational motions are relaxed to low temperatures 10–50 K, as relevant for comparison with astronomical observations are presented. Mass-selected ions are constrained in a 22-pole ion trap where the vibrational and rotational degrees of freedom are relaxed by collisions with cryogenically cooled helium gas. This investigation is on a $C_6H_6^+$ isomer, 2,4-hexadiyne cation, and utilizes 1-photon predissociation to record its $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ electronic spectrum. The well resolved vibrational pattern and the K-rotational structure on the origin band indicate an internal temperature in the 20–30 K range and leads to the mapping of the excited state vibrational levels.

Keywords: Electronic spectra; Cold-cations; Ion trap; Interstellar-absorption; Organic cation

1. Introduction

One of the challenges related to astronomical observations, in particular of absorptions in diffuse interstellar clouds, is to measure in the laboratory the electronic spectra of larger and transient ions where not only the rotational but also vibrational degrees of freedom have been equilibrated to low temperatures. Once these become available, a direct comparison of the two sets of data can be made [1] with the objective of identifying the carriers. A number of such studies have proven possible in the last decade by producing cold smaller polyatomic cations in pulsed discharge sources and measuring their electronic absorption spectra with sensitive techniques such as cavity ring-down with pulsed and cw lasers [2]. The species could be identified by analysis of the rotational structure in the spectra and/or previous knowledge on the location of these electronic transitions from absorption measurements of mass-selected species in neon matrices [3]. In the case of anions, and transient neutral species, identification of the molecules can be made by mass-selection using multi-photon dissociation processes.

The usual approaches to study the electronic spectra of cold ions in the gas phase have used molecular beams. This leads to low rotational temperatures but not all vibrational modes are relaxed. For this reason some experiments have been carried using ions cooled to liquid nitrogen temperatures for laser induced fluorescence [4] or photodissociation studies [5]. Another interesting way to improve the quality of such spectra has been used tagging methods [6], whereby a rare gas is attached to the parent ion. The spectra can become significantly sharper, but the rare gas causes a shift in transition energies compared to the bare ion [7].

Thus the goal of the present experiment is to relax both the rotational and vibrational motions by collisions to low temperatures as pertinent to the interstellar medium, e.g., 10–50 K. In this mass-selected ions are injected into a 22-pole radio-frequency trap where they are brought to the low temperatures by collisions with cryogenically cooled helium gas [8]. The electronic absorption is induced by tunable laser excitation and the process is detected by production of fragment ions either in one or several photon processes.

Whether the cooling has been achieved can be shown on small ions by the resolution of the rotational structure (e.g., N_2O^+ in Ref. [8]) but for the larger organic ions such structure is not resolved. This has been circumvented in this study by choosing an ion with K-structure, i.e., a system with hydrogen atoms off a central carbon chain axis, which can be observed with modest laser resolution 2,4-hexadiyne cation is the example chosen enabling the rotational temperature to be determined.

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It was important to show that also such large ions are efficiently cooled in the trap and the proof is provided here.

Related approaches employing photodissociation have been carried out in the past using icr or tandem mass-spectrometers [9,10], though cooling by collisions with helium atoms to low temperatures as 10–20 K was not implemented, and most of the experiments sampled ions with not well defined internal energy [11]. However, this is a crucial aspect for the measurements aimed at astronomical observations. In order to demonstrate the approach, a large organic cation was chosen, 2,4-hexadiyne isomer of $C_6H_6{}^+$, because its electronic spectrum, $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition, has been characterized in molecular beams in emission [12], by laser induced fluorescence [13], and the excited electronic state leads to fragmentation. Precisely, on formation of the upper state, there is competition between fluorescence to the ground state and dissociation. Both these decay channels have been studied; one by determination of the fluorescence quantum yield [14] and the other via branching ratios of fragment ions [15]. For example on production of the ion in the lowest vibrational level of the excited ^2E_u state, ~74% of the time the ion falls back down to the ground $\tilde{X}^2E_g$ state, and the rest fragments to produce dominantly $C_6H_5{}^+$ with minor amounts of $C_6H_4{}^+$ and $C_4H_4{}^+$. As the measured breakdown curves show, the yield of $C_6H_5{}^+$ and $C_4H_4{}^+$ remains constant (around 0.20 and 0.05, respectively) on increasing the internal energy in the ^2E_u state by around 4000 cm^{-1} [14].

Because the ion is a symmetric top (with assumed D_{3h} symmetry) the K-structure (rotation around the carbon containing axis) within the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition can be observed with modest resolution, enabling the temperature to be read-off from the spectrum. By this means the viability and the concept of the approach has been tested and the results are presented here. Most striking is the improvement in quality of the spectrum showing numerous narrow vibronic bands with increasing complexity as the upper states are accessed, in part due amplification of weaker bands by saturation. This new spectroscopic information on the vibrational manifold in the $\tilde{A}^2E_u$ excited electronic state is presented.

2. Experimental

The experiment was carried out at 10 Hz repetition rate. Fig. 1 shows the overall lay-out of the apparatus. Solid C_6H_6 was placed in a stainless steel oven which was heated to 40 °C by a resistive wire. The vapor flowed through a 0.5 mm orifice after which ~10 eV electron impact ionization took place. The pressure there was around 4×10^{-6} mbar. The $C_6H_6{}^+$ ions were then mass-selected by a quadrupole filter and injected into a 22-pole ion trap, of 3 cm length and 10 mm in diameter, built according to the principles described [16]. The ions are constrained in the trap by a RF field and undergo collisions with helium gas cooled by a cryostat operating at 6 K. After 71 ms in the trap (Fig. 2) the ions are irradiated by a laser pulse (typically 3 mJ) coming from a tunable laser system (OPO) with 0.3 cm^{-1} bandwidth. A dye laser system was used for the higher resolution (0.03 cm^{-1}) measurements.

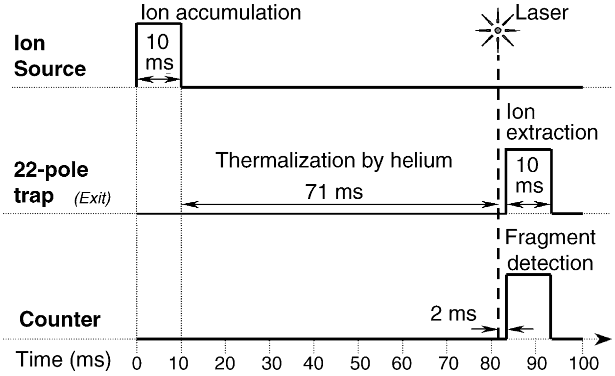

Fig. 2. Timing and pulse sequence for the measurements carried out at 10 Hz.

Following the laser excitation the potential on the exit of the ion trap is lowered. This allows the fragment ions to be separated from the $C_6H_6{}^+$ parents by a further quadrupole mass filter operating with almost unity resolution. Each detected ion produces a uniform spike (5 ns, 5 V) on the discriminator output sent to a 300 MHz counter. The number of fragment ions is counted as a function of the laser wavelength to provide the absorption spectrum. The spectrum is normalized for photon intensity, monitored shot to shot by a photodiode. Each data point is an average of 50 cycles.

3. Results and discussion

3.1. Internal temperature of 2,4-hexadiyne cation

The electronic absorption process was monitored via the fragmentation channel leading to $C_6H_5{}^+$, $C_6H_4{}^+$ and $C_4H_4{}^+$. Fig. 3 shows the spectrum in the 20,000–22,850 cm^{-1} range recorded by monitoring the number of $C_4H_4{}^+$ counts as function of laser frequency (0.3 cm^{-1} bandwidth). The relative intensities of the vibronic bands differ somewhat for reasons discussed in the next section. The origin band at 20,553 cm^{-1} stands alone and there is no evidence of hot bands of type ν_1^0 or ν_2^0 to lower energy, or sequence transitions ν_1^1 arising from residually populated vibra-

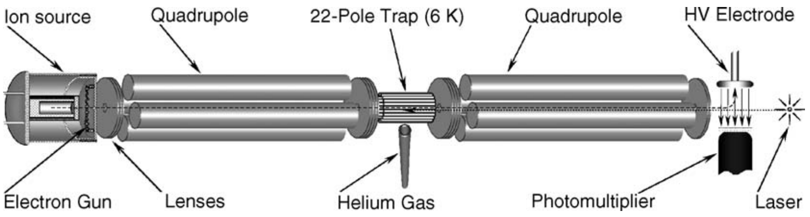

Fig. 1. Schematic outlay of the apparatus based on a 22-pole ion trap.

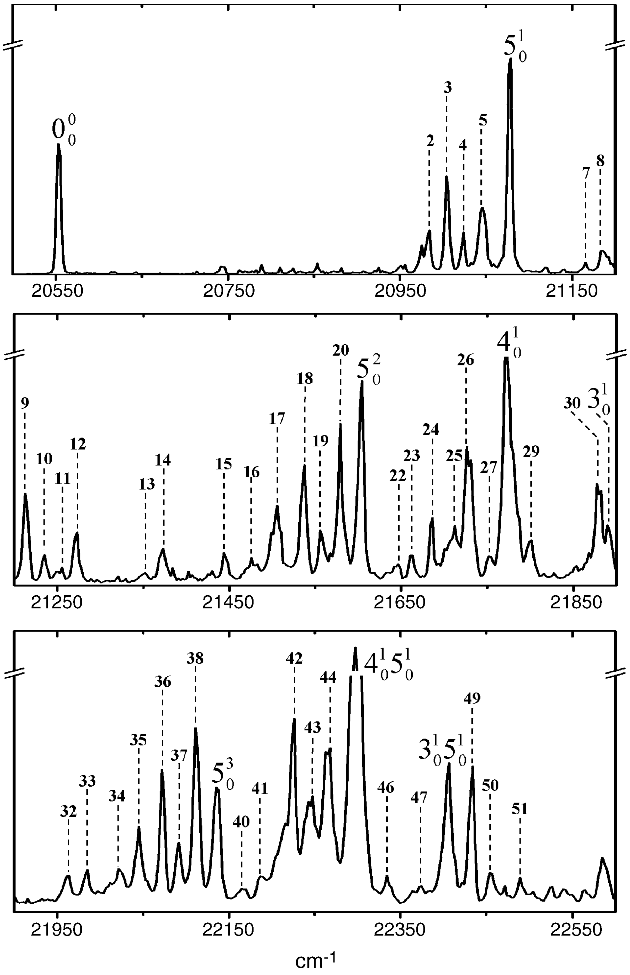

Fig. 3. The $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition of 2,4-hexadiyne cation recorded ($0.3\,cm^{-1}$ resolution) via a one-photon predissociation process by monitoring the $C_4H_4^+$ fragment ions produced. The ions were vibrationally and rotationally relaxed to around 30 K by collisions with cryogenically cooled helium in a 22-pole radio-frequency trap.

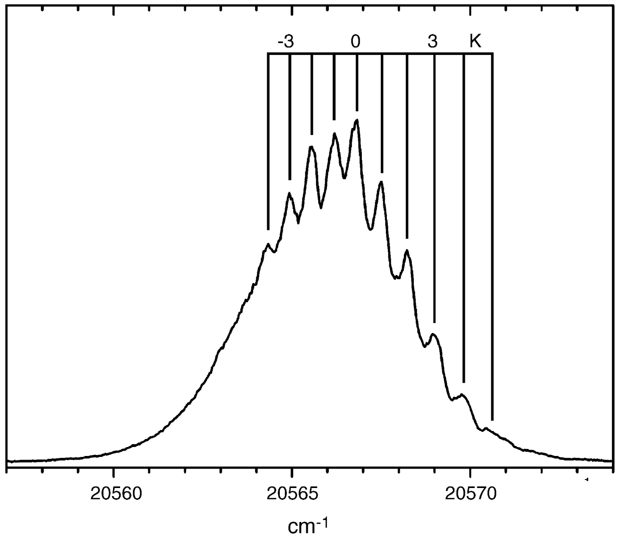

Fig. 4. The origin band in the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition of 2,4-hexadiyne cation detected via predissociation to $C_4H_4^+$ using a laser bandwidth of $0.03\,cm^{-1}$. The assignment of the K-structure is taken from [17] and the intensity distribution corresponds to a rotational temperature in the 20–30 K range.

tional levels in the $\tilde{X}^2E_g$ ground state. The lowest frequency mode is around $120\,cm^{-1}$ and thus the vibrational temperature is below 30 K. When the laser bandwidth is reduced to $0.03\,cm^{-1}$ the rotational structure due to the K-stacks is resolved. This is seen in Fig. 4 together with the quantum number assignment inferred in the analysis of the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ emission spectrum [17]. This pattern varies with temperature and the spectrum shown in Fig. 4 resembles closely the top two traces of Fig. 2 in Ref. [17], i.e., a rotational temperature in the 20–30 K range. In a spectroscopic study of the related molecular ion, of 1,3-pentadiyne, more details of the rotational temperature dependence on the expansion backing pressure are explicitly given [18]. The vibrational and rotational degrees of freedom are thus equilibrated to around 20–30 K.

3.2. Vibrational structure

The electronic spectrum shows increasing complexity as the laser excitation frequency is increased. Whereas in the spectrum reported earlier using ions relaxed to about 150 K and recorded via a laser induced fluorescence technique [13], only the totally symmetric modes (ν_1 to ν_5) appear to be strongly excited, many more transitions are now apparent (Fig. 3). In Table 1 the frequencies of all the observed distinct peaks in the spectrum are listed with numbering as shown in Fig. 3. All these are new observations leading to a detailed mapping of the $\tilde{A}^2E_u$ exited electronic state manifold.

The strongest bands involve the totally symmetric modes 5^1_0, 4^1_0 and their combinations. There are too many other bands to be assigned only to transitions involving the five a_{1g} modes where the D_{3h} symmetry is retained in both electronic states, which have the frequencies of 2911, 2266, 1378, 1255 and $560\,cm^{-1}$ in the ground state of neutral 2,4-hexadiyne [19]. For example, four distinct peaks lie just below the 5^1_0 transition (i.e., $<500\,cm^{-1}$) which have to correspond to the excitation of the degenerate modes in two, or more, quanta. These can only be constructed from the four degenerate modes ν_{14} ($350\,cm^{-1}$), ν_{15} ($121\,cm^{-1}$) both of e_u symmetry, and ν_{20} ($245\,cm^{-1}$) of e_g, where the frequencies given are the values of the neutral molecule. Thus the $14^1_0 15^1_0$, 15^2_0, 20^2_0 transitions would each give a totally symmetric level as would 15^4_0 with several components with energies below $500\,cm^{-1}$. The number of such peaks increases with internal energy as more possibilities arise for the formation of totally symmetric levels by appropriate combinations of the degenerate modes, but a specific assignment would not be unambiguous. For this reason in Table 1 only the evident progressions and combinations involving totally symmetric modes are given.

The enhanced intensity of the transitions involving the degenerate modes is a result of saturation. This is illustrated in Fig. 5 where the region around the 5^1_0 transition is recorded: trace (a)—using the same laser power as in Fig. 3, and (b) attenuated by a factor of around 300. The latter measurement is a reflection of a normal absorption; the bands arising from the excitation of the degenerate modes are quite weak and reflect the Franck–Condon factors. At the higher laser density these

Table 1
Wavenumbers of vibronic bands in the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ system of 2,4-hexadiyne cation

No.	Band wavenumber (cm^{-1})	Relative to 0_0^0 (cm^{-1})	Assignment
1	20553	0	0_0^0
2	20984	431	
3	21004	451	
4	21024	471	
5	21046	493	
6	21079	526	5_0^1
7	21166	613	
8	21183	630	
9	21213	660	
10	21235	682	
11	21255	702	
12	21273	720	
13	21352	799	
14	21373	820	
15	21443	890	
16	21475	922	
17	21505	952	
18	21538	985	
19	21556	1003	
20	21579	1026	
21	21605	1052	5_0^2
22	21647	1094	
23	21663	1110	
24	21686	1133	
25	21712	1159	
26	21726	1173	
27	21754	1201	
28	21773	1220	4_0^1
29	21801	1248	
30	21877	1324	
31	21889	1336	3_0^1
32	21961	1408	
33	21985	1432	
34	22021	1468	
35	22045	1492	
36	22072	1519	
37	22092	1539	
38	22111	1558	
39	22135	1582	5_0^3
40	22165	1612	
41	22187	1634	
42	22226	1673	
43	22248	1695	
44	22268	1715	
45	22297	1744	$4_0^1 5_0^1$
46	22334	1781	
47	22374	1821	
48	22407	1854	$3_0^1 5_0^1$
49	22434	1881	
50	22457	1904	
51	22489	1936	

The numbering of the peaks is that shown in Fig. 3.

weak transitions are saturated leading to increased intensities. At even higher powers (tens of mJ per pulse) the peaks in the spectrum broaden. The inset of Fig. 5 shows the intensity of the 5_0^1 band plotted as function of the laser power. The non-linear dependence indicates saturation above 0.5 mJ/pulse. By this means the manifold of the vibration levels in such cold polyatomic ions is “lit-up”.

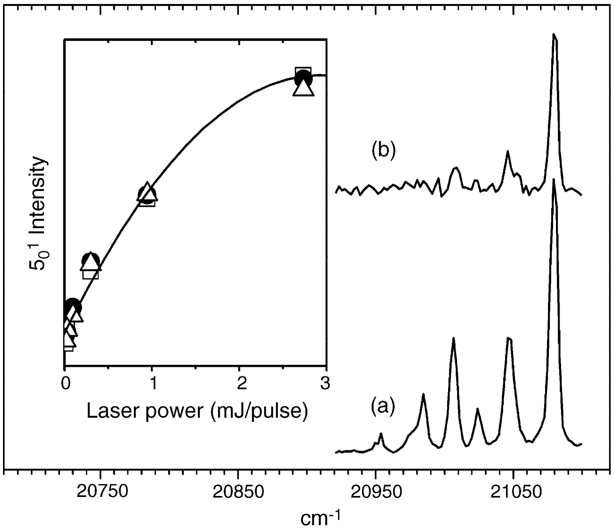

Fig. 5. The region around the 5_0^1 transition in the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ of 2,4-hexadiyne cation detected via predissociation to form $C_4H_4^+$ recorded: (a) at 3 mJ/pulse (as in Fig. 3), (b) at 9 μJ/pulse (∼300 times lower). The inset shows the dependence of the 5_0^1 band on laser energy indicating that the transition is saturated.

4. Conclusion

The analysis of the rotational K-structure resolved on the origin band of the $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition of 2,4-hexadiyne cation, and the absence of sequence vibrational bands, indicate that the approach developed to study the electronic spectra of larger polyatomic cations which have been collisionally relaxed to temperatures relevant to the interstellar medium is successful. In the present case the vibrational and rotational degrees of freedom are equilibrated to 20–30 K. The system studied here was selected because one-photon transitions were known to lead to fragmentation from the excited electronic state and the K-structure was resolvable. The richness of the vibronic spectrum is obtained by saturating the weak transitions and thus may be used to deduce vibrational frequencies in the excited electronic state in larger, cold ions.

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References

[1] T. Motylewski, H. Linnartz, O. Vaizert, J.P. Maier, G.A. Galazutdinov, F.A. Musaev, J. Krelowski, G.A.H. Walker, D.A. Bohlender, Astrophys. J. 531 (2000) 312.

[2] See for example;
D. Khoroshev, M. Araki, P. Kolek, P. Birza, A. Chirokolava, J.P. Maier, J. Mol. Spectrosc. 227 (2004) 81, and references therein.

[3] J.P. Maier, J. Phys. Chem. A 102 (1998) 3462.

[4] See for example;
T.A. Miller, V.E. Bondybey (Eds.), Molecular Ions: Spectroscopy, Structure, and Chemistry, North-Holland, Amsterdam, 1983.

[5] D. Nolting, C. Marian, R. Weinkauf, Phys. Chem. Chem. Phys. 6 (2004) 2633.
[6] M.A. Duncan, Int. Rev. Phys. Chem. 22 (2003) 407.
[7] T. Pino, N. Boudin, P. Brechignac, J. Chem. Phys. 111 (1999) 7337.
[8] A. Dzhonson, E. Bieske, D. Gerlich, J.P. Maier, J. Mol. Struct., in press.
[9] R.C. Dunbar, Int. J. Mass. Spectrom. 200 (2000) 571.
[10] M.A. Duncan, Int. J. Mass. Spectrom. 200 (2000) 545.
[11] D. Rolland, A.A. Specht, M.W. Blades, J.W. Hepburn, Chem. Phys. Lett. 373 (2003) 292.
[12] D. Klapstein, S. Leutwyler, J.P. Maier, Chem. Phys. Lett. 84 (1981) 534.
[13] J.P. Maier, L. Misev, Chem. Phys. 51 (1980) 311.
[14] P. Forster, J.P. Maier, F. Thommen, Chem. Phys. 59 (1981) 85.
[15] J. Dannacher, Chem. Phys. 29 (1978) 339.
[16] D. Gerlich, Adv. Chem. Phys. 82 (1992) 1.
[17] D. Klapstein, R. Kuhn, S. Leutwyler, J.P. Maier, Chem. Phys. 78 (1983) 167.
[18] S. Leutwyler, D. Klapstein, J.P. Maier, Chem. Phys. 78 (1983) 151.
[19] C.J. Nielsen, Spectrochim. Acta 39A (1983) 993.