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Double Resonance Rotational Spectroscopy of Weakly Bound Ionic Complexes: The Case of Floppy CH_3^+-He

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A novel rotational spectroscopy method applicable to ions stored in cold traps is presented. In a double resonance scheme, rotational excitation is followed by vibrational excitation into a dissociative resonance. Its general applicability is demonstrated for the CH_3^+-He complex, which undergoes predissociation through its C-H stretching modes ν_1 and ν_3. High resolution rotational transitions are recorded for this symmetric top, and small unexpected splittings are resolved for $K = 1$. Advantages and potential future applications of this new approach are discussed.

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To date, one of the most successful approaches for the elucidation of molecular ions is action spectroscopy, in which laser or mm-wave irradiation is applied to a mass-selected ensemble of trapped (or guided) ions. Its very high sensitivity derives from counting ions as the spectroscopic signal (and not detecting light as in conventional methods). In particular, for weakly bound ionic complexes such as $H^+(H_2O)_n$, $CH_5^+(H_2)_n$ or $H_3^+(H_2)_n$, the action spectroscopic method called "vibrational predissociation" has been the standard technology for decades [1–6]. With this method, charged complexes are first mass selected and then excited by IR photons into a resonant vibrational state above the lowest dissociation limit, and subsequent dissociation signals the photon absorption. A nonzero lifetime of these resonant states leads to fairly resolvable (ro)vibrational lines and thus to the determination of molecular structure. In the so-called messenger (or tagging) variant, a very weakly bound rare gas atom or light molecule (e.g., H_2) is attached to a stable ion under investigation [6–11], with the photodissociation leading to loss of the tag. In the limit of large cations and weakly interacting tags (e.g., He), only a minor perturbation is imposed on the core ion, rendering this approach a valuable tool when other vibrational action spectroscopic methods are not available [7,8,11–13]. In this work, we propose a novel method capable of extending the field of photodissociation into the regime of rotational spectroscopy by using a double resonance scheme (Fig. 1). Utilizing destruction of the molecular ion (complex) through a resonant state, the proposed scheme is of general applicability. As such, it complements existing (double resonance) rotational action spectroscopic schemes for ions [14–20]. We demonstrate its feasibility for the disk-and-ball CH_3^+-He complex, which has been chosen because of its presumable simple spectrum (closed shell symmetric top), its large dipole moment (2.9 D [21]), and because its ν_3 band

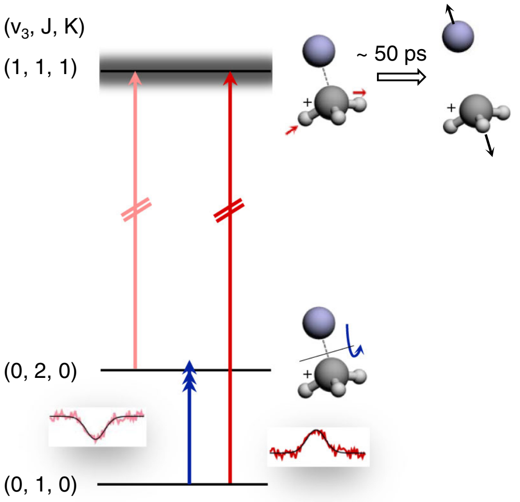

FIG. 1. Rotational-predissociation double resonance scheme illustrated for the example of CH_3^+-He. The fixed IR laser probes either the initial (dark red) or the final level (light red) of the rotational transition (blue), giving rise to different signal forms when the frequency of the rotational excitation is scanned. In the left-hand combination, the rotational transition pumps ions into the level (0, 2, 0) probed by the IR laser, enhancing the destruction of CH_3^+-He. In the right-hand combination, the rotational transition pumps ions out of the level (0, 1, 0) probed by the IR laser, thus hindering the destruction.

(antisymmetric C-H stretch) is already known [7,22]. Because of the cryogenic experiment, highly resolved rotational lines can be obtained and, thus, effects of large amplitude zero-point motion discovered.

The experiments are performed in the 22-pole ion trapping machine COLTRAP [23]. CH_3^+ ions are created in a storage ion source by electron impact ionization of methane (Linde 5.5). At the beginning of each experimental cycle, an ion pulse (40 ms) is extracted from the source, mass filtered for CH_3^+ ($m = 15\ u$), and injected into the 22-pole ion trap [24]. On entrance, the ions are cooled by collisions with He buffer gas, which is injected via a piezovalve a few ms before arrival of the ions. Because of the high He number density and low trap temperature (4 K), around 8000 CH_3^+-He complexes are formed via ternary collision processes. During the storage time of typically 1.7 s, these ions are exposed to a cw infrared laser beam, leading to IR photodissociation (IRPD) upon resonant absorption:

$$CH_3^+\text{-He} \xrightarrow{h\nu} [CH_3^+\text{-He}]^* \longrightarrow CH_3^+ + \text{He}. \qquad (1)$$

After the trapping period, the trap content is extracted and mass filtered for CH_3^+-He ions ($m = 19\ u$), which are then detected by an ion counter. Predissociation spectra are recorded by counting the number of CH_3^+-He complexes as a function of the laser frequency. A laser shutter allows for normalization of the detected ion counts to the number of ions without laser irradiation.

For the double resonance rotational spectroscopy scheme in Fig. 1, a tunable narrow-bandwidth (sub)mm-wave beam is overlapped with the laser beam via an elliptical mirror with a 3 mm hole [17]. For this scheme, the laser frequency is stabilized on a predissociating transition to obtain a constant IRPD signal. Depending on the choice of the rotational transition linked with the vibrational transition, either depletion or enhancement of the signal intensity is obtained, when the (sub)mm-wave source is tuned through the rotational resonance.

The obtained IRPD spectra are summarized in Fig. 2. Because of the nominal trap temperature of 4 K, only the lowest rotational levels $J'' = 0$–5 are probed. The perpendicular ν_3 band in Fig. 2(a) features five unresolved Q branches in the range 3094–3134 cm^{-1}, and 24 resolved rovibrational P and R branch lines. The lines are lifetime broadened (the laser linewidth is negligible and the laser power is limited to 20 mW to avoid power broadening). Thus, they are fitted with Lorentzians to determine center frequency and linewidth (FWHM), which corresponds to a lifetime of ≈16–48 ps in the ν_3 state. The assigned line list and comparison to former work [7] is given in the Supplemental Material [25], which includes Refs. [26,27]. Fading of the P branch lines at the low frequency end of the spectrum results from the rotational population distribution, which corresponds to $T_{\text{rot}} = 9.4 \pm 0.3$ K.

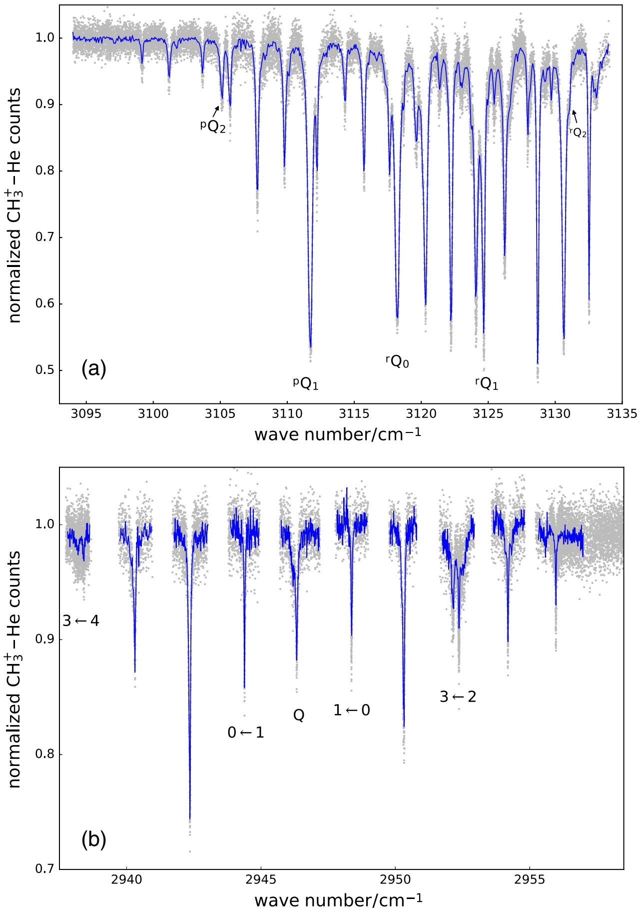

FIG. 2. IRPD spectra of (a) the ν_3 antisymmetric and (b) ν_1 symmetric C-H stretch of CH_3^+-He. The data (gray dots) are normalized and binned in 0.01 cm^{-1} steps (blue lines). (a) The ν_3 band is a perpendicular transition, and was measured previously [7]. In total, 24 P and R branch transitions are resolved. The five unresolved Q branches are annotated by $^{\Delta K}\Delta J_K$. The applied power is ≈20 mW. (b) Ten partly unresolved features are recorded for the parallel ν_1 band, with the Q branch at 2946.33 cm^{-1}. The splitting of the $J = 3 \leftarrow 2$ and $3 \leftarrow 4$ transitions indicates a perturbation in the upper $J' = 3$ state. Since ν_1 is only weakly IR active, a laser power of around 400 mW is applied.

The totally symmetric ν_1 fundamental is IR forbidden for bare CH_3^+. It becomes weakly IR active for CH_3^+-He, because of the pyramidal deformation upon complexation (deviation from planarity 1.4° [7,22]). Searches in the 2914–2980 cm^{-1} range with high laser power result in the single band depicted in Fig. 2(b). The assignment to the ν_1 mode is confirmed by its parallel structure (line list in Supplemental Material [25]). Most of its rovibrational lines are blended, the $(J,K) = (0,0) \leftarrow (1,0)$ and $(1,0) \leftarrow (0,0)$ transitions being the only isolated ones. A fit of these lines with Lorentzians yields a lifetime of ≈130 ps. Thus, the ν_1 state lives longer than the ν_3 state, probably because of a less effective mode coupling of ν_1 into the dissociative C-He stretching motion. A perturbation in the ν_1 state results in a splitting of the rotational lines with $J' = 3$.

Similar perturbations with splittings for selected J' levels were previously observed for HCO^+-He [8], N_2H^+-Ne [28], and NH_3^+-Ar [29].

For double resonance spectroscopy, the ν_3 band is chosen, due to its intense and well separated rovibrational transitions. Both double resonance schemes shown in Fig. 1 are applied. With the predictions from the IR work, the rotational transitions listed in Table I are found. For these measurements, the trap temperature is adjusted between 4 and 10 K to increase the population of the probed lower states. Also, care is taken to avoid broadening and skewing of the lines observed at excessive mm-wave power. As shown for the example measurements in Fig. 3, $K = 1$ transitions of this symmetric top exhibit an unexpected splitting of the order of 1 MHz, which increases with J. This splitting points to a perturbation, which effectively renders the Hamiltonian to be formally that of a slightly asymmetric top. A corresponding fit (in S reduction) yields good agreement, with a tiny asymmetry of $\kappa = (2B - A - C)/(A - C) = -0.999\,996$. Such a near symmetric top exhibits noticeable splittings only for $K = 1$, whereas levels with $K = 0$ and $K \geq 2$ have no and negligible splittings, respectively. The derived spectroscopic parameters for all states are listed in Table II, showing good agreement with the values determined earlier for the ground and ν_3 states [7]. Although sextic and octic distortion constants are included in our ground state fit, it converges poorly, with oscillating observed-calculated values in Table I and an average deviation of 1.7σ (or 10 kHz). We expect such behavior to be a regular feature for all loosely bound cation-He complexes.

It is difficult to explain the observed splitting by an asymmetry of the molecule, as quantum chemistry calculations [7,22] indicate that the global minimum of the potential energy surface locates at the C_{3v} structure. The observed phenomenon is most probably caused by the large amplitude motion of the He atom in the ground vibrational state. Olkhov *et al.* [7] estimate that the He atom is located on average about 10° off from the C_3 symmetry axis. Because of this delocalization, the energy levels of the ground state resemble those of an asymmetric top, the splitting being caused by the internal rotation of the CH_3 moiety [32]. Whereas equally intense K-type doublets are expected for an asymmetric top, unequal intensity ratios are observed in the present case, as shown in Fig. 3 and listed in Table I. Since we found no systematic tendency in the observed intensity ratios, it may be caused by the difference in transition strength or photodissociation efficiency. Interestingly, level splittings arising from He tunneling

TABLE I. Rotational transitions of CH_3^+-He (in MHz, uncertainties in parentheses) measured with the double resonance method.

$(J', K') \leftarrow (J'', K'')$	This work	Observed-calculated	Intensity ratio[a]
$(1,0) \leftarrow (0,0)$	60 173.4502(23)	−0.0046	
$(2,0) \leftarrow (1,0)$	120 158.8392(25)	−0.0037	
$(2,1) \leftarrow (1,1)$	120 203.2878(34)	0.0026	1
	120 203.7499(28)	−0.0041	1.19
$(3,0) \leftarrow (2,0)$	179 766.1580(7)	0.0003	
$(3,1) \leftarrow (2,1)$	179 832.9310(35)	0.0025	1
	179 833.7427(22)	0.0050	1.3
$(3,2) \leftarrow (2,2)$	180 035.9360(14)	−0.0013	
$(4,0) \leftarrow (3,0)$	238 801.3393(28)	0.0033	
$(4,1) \leftarrow (3,1)$	238 890.5685(81)	0.0094	1
	238 891.8624(54)	0.0011	0.85
$(4,2) \leftarrow (3,2)$	239 162.3390(37)	0.0125	
$(4,3) \leftarrow (3,3)$	239 614.5071(97)	0.0033	
$(5,0) \leftarrow (4,0)$	297 063.7827(22)	−0.0063	
$(5,1) \leftarrow (4,1)$	297 175.6186(24)	−0.0024	1
	297 177.6496(45)	−0.0128	0.47
$(5,2) \leftarrow (4,2)$	297 517.1498(40)	−0.0074	
$(5,3) \leftarrow (4,3)$	298 085.3671(219)	−0.0136	
$(6,0) \leftarrow (5,0)$	354 343.4083(19)	0.0041	
$(6,1) \leftarrow (5,1)$	354 478.0512(173)	0.0241	1
	354 481.2005(104)	0.0167	1.27
$(6,2) \leftarrow (5,2)$	354 890.7012(93)	0.0102	
$(7,0) \leftarrow (6,0)$	410 416.8161(94)	−0.0247	

[a] The relative intensity of the K-doublet components is listed where the intensity of the lower component is set 1.

TABLE II. Spectroscopic parameters for CH_3^+-He. Band origins are given in cm^{-1}, and all other parameters in MHz. Uncertainties are given in parentheses.[a]

	Ground	ν_1	ν_3
ν		2946.386(4)	3115.583(5)
A	143844(97)	142 498(377)	142 603(65)
$\bar{B}$	$\mathbf{30\,102.368(1)}$	29 837(40)	29 815(16)
$B - C$	$\mathbf{0.209(6)}$		
D_J	$\mathbf{7.8150(1)}$	8.8(15)	8.4(3)
D_{JK}	$\mathbf{-11.128(1)}$		−10.8(18)
D_K	12.6(98)		7.6(53)
d_1	$\mathbf{0.0008(1)}$		
H_J	$\mathbf{-2.607(3)\times 10^{-3}}$		
H_{JK}	$\mathbf{2.55(3)\times 10^{-3}}$		
H_{KJ}	$\mathbf{22.3(3)\times 10^{-3}}$		
h_1	$\mathbf{6(2)\times 10^{-6}}$		
L_J	$\mathbf{-4.37(3)\times 10^{-6}}$		
L_{JJK}	$\mathbf{3.8(5)\times 10^{-6}}$		
L_{JK}	$\mathbf{4.2(4)\times 10^{-5}}$		
L_{KKJ}	$\mathbf{-0.00162(2)}$		

[a] Spectroscopic fit was done with the program PGOPHER [30]. First, only the ground state was simulated, applying an asymmetric top model to the data in Table I, yielding an average deviation of 1.7σ (or 10 kHz). The resulting parameters are printed bold. With the ground state parameters fixed and converted into a symmetric top ($B - C = 0$), ν_1 and ν_3 have been treated. Because of the perturbation and limited number of lines in ν_1, only few parameters could be retrieved. The fit has been done by setting $\zeta_3 = 0.11$ [31].

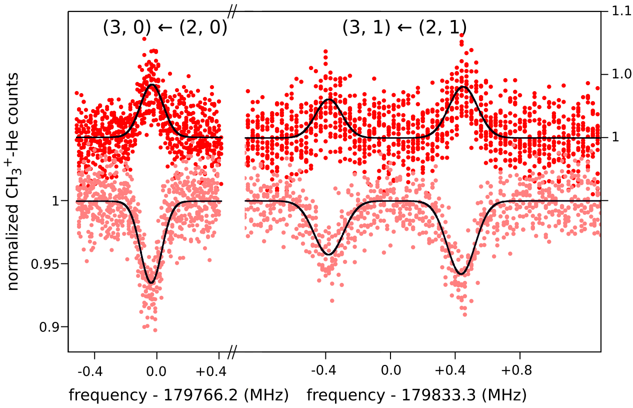

FIG. 3. Four single measurements of rotational ground state transitions at a nominal trap temperature of 4 K. The color code (light and dark red) corresponds to the two measurement schemes illustrated in Fig. 1. The small splitting for the $K = 1$ transition is explained in the text.

between both sides of planar CH_3^+, predicted to be of the order of 0.001 cm^{-1} [22], are not detected.

The presented double resonance scheme is widely applicable. The only requirements are long-lived resonances, so that individual rovibrational transitions can be addressed by the IR laser. For example, this novel rotational approach has recently been applied to the linear HCO^+-He complex in the Cologne laboratory [33], based on former IR work [8]. Advantages of this method are the inherent verification of the assignments of the probed IR and mm-wave transitions, as well as the high resolution achieved for Doppler-limited rotational lines measured in cryogenic experiments. Such a high resolution is prevented by lifetime broadening in bare predissociation spectra (indicated in Fig. 1 for the dissociating level). On the other hand, the broadened IR lines are beneficial in double resonance experiments, because the requirements for laser stabilization are less strict. Other (action) spectroscopic methods for measuring rotational spectra of weakly bound complexes are less suitable. For instance, we failed to measure rotational transitions of CH_3^+-He and HCO^+-He with the method of state-selective attachment of He atoms [18], in which attachment of a second He atom to form CH_3^+-He_2 (or HCO^+-He_2) is hindered by mm-wave excitation.

Future challenging targets of this new method are complexes like H_3^+-He [34] or H_2^+-He. In particular, H_2^+-He is interesting, because no conclusive spectroscopic data exist for this fundamental three-electron system, and only *ab initio* data are available for its rovibrational levels [35]. Also, this rather strongly bound complex may have played an important role in the early Universe.

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