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Ground state of $CH_2{}^+$: Experimental aspects and theoretical implications

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Hot $CH_2{}^+$ molecular ion ensembles were prepared, accelerated, and stored for radiative cooling to room temperature. The structure of the species was measured by the Coulomb explosion imaging method at different stages of cooling. The bending angle distributions were extracted and compared with recent theories as well as a previous Coulomb explosion imaging measurement. The comparison reveals an apparent large nonadiabatic contribution to the low-lying $CH_2{}^+$ wave functions. [S1050-2947(99)02403-8]

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The $CH_2{}^+$ has been the most quoted example of the Renner-Teller effect where the degeneracy of the linear $^2\Pi_u$ electronic ground state is removed by vibronic coupling producing a bent $\tilde{X}^2A_1$ ground state and a linear $\tilde{A}^2B_1$ first excited state. This had been the basis for all theoretical treatment and experimental interpretation of low-lying vibrational $CH_2{}^+$ states. The purpose of this paper is to disclose data on the structure of $CH_2{}^+$, which demonstrates the inadequacy of this standard interpretation of vibrations of small linear molecules.

The recently developed experimental technique utilizing a combination of a storage ring and the Coulomb explosion imaging method (CEI) is shortly described in the next paragraphs and more details can be found in Ref. [1]. The findings discussed here are the bending angle distributions of ensembles of $CH_2{}^+$ ions at different excitation levels. The bending angle distribution of the grand-canonical ensemble at 300 K is a particular example. Simple theoretical arguments show that the distribution measured at 300 K must be very close to the square of the Born-Oppenheimer vibrational ground-state wave function. A comparison of the data to such an expectation will be shown. A closer look into adiabatic approximation theories reveals a major deviation from the simple expectation. The experimental findings are found incompatible with such adiabatic theories. The major evidence is the discrepancy between theory and experiment for the density near the linear conformation. A further evidence is the systematic behavior of the density at different measured excitation levels. Apparently, an inevitable conclusion from the experimental results is that the wave functions of $CH_2{}^+$ low-lying states must include large nonadiabatic contributions beyond the Renner-Teller description.

Experiments where molecular ions are stored in a storage ring at a relatively high velocity ($v/c \sim 0.03$) and extracted after various storage times to a CEI device are being carried out at the Max Planck Institut für Kernphysik–Heidelberg in collaboration with the Weizmann Institute–Rehovot. A detailed description of such experiments is given elsewhere [1]; only specific features of the current experiment on the structure of $CH_2{}^+$ are described below.

A beam of CH_3O^- was produced from CH_3OH vapor in a Cs sputter source and injected into a tandem accelerator. A gas stripper was used and the $CH_2{}^+$ fraction at 6.69 MeV was magnetically analyzed and injected into the storage ring [2]. Stored molecular ions were extracted continuously to the CEI beam line where single molecules were measured at a maximum rate of 25 Hz. A formvar target, 80 ± 10 Å thick, was used for the CEI stripping process. The resulting fragments were magnetically deflected to a set of two time-position (3D) sensitive detectors so that protons were collected by one detector while the carbon fragments with charge states $q=+3$ and $q=+4$ were deflected to the second detector. These charge states constitute the two largest components of the charge-state distribution with a slightly higher rate for the $q=+4$ component.

The $CH_2{}^+$ ions were produced by hard collisions of 4.68 MeV CH_3O^- ions with the stripper gas at the terminal of the tandem. Thus, it is expected that the $CH_2{}^+$ ions were highly excited when injected into the storage ring. By the time these ions were extracted, they underwent several radiative processes which lowered their excitation levels. This storage time, t_s, is monitored when the molecule is detected. The ensemble of molecules arriving before the Coulomb explosion stripper foil at a given storage time can be characterized by the population of the different molecular states at that time. The density function of nuclear conformations, $\mathcal{D}(R,t_s)$, is simply the sum of the nuclear conformation density functions of each state weighted by the population of each state at the time t_s. The space of these nuclear conformations is defined here as the R space. Upon collision with the stripper foil, the molecular Hamiltonian switches suddenly, within 10^{-16} sec, to individual atomic ions interacting Coulombically. The nuclear conformations density function $\mathcal{D}(R,t_s)$ develops in time under the influence of the new Coulomb Hamiltonian where it transforms into an asymptotic density $\mathcal{D}_v(V,t_s)$—the density of configurations in the asymptotic velocity space. This space is defined here as the V space. The density $\mathcal{D}_v(V,t_s)$ is sampled by the CEI detectors which measure the V-space configurations of individual molecular ions.

The raw experimental data are a sample of three-dimensional nuclear conformations in V space (nine dimen-

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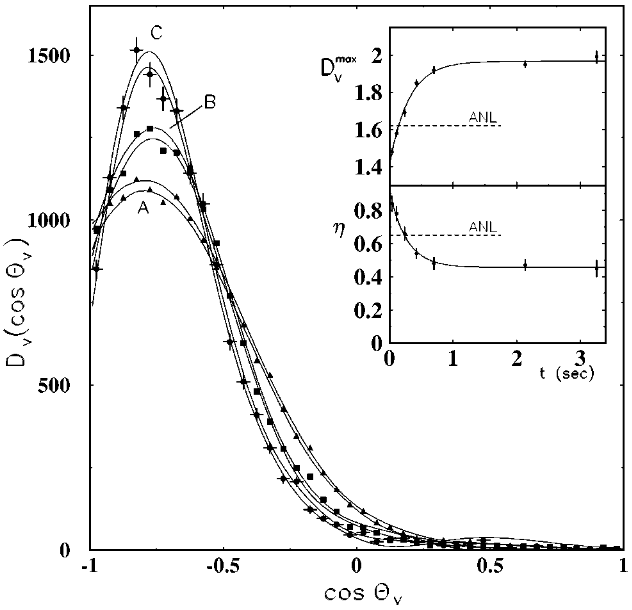

FIG. 1. V-space angular distributions at three different storage times: 0–100 msec (A), 200–350 msec (B), 3–4 sec (C). Both histograms and fits are shown. The histogram of the latest time interval (C) is shown with representative error bars. The double lines represent the limits on the fitting functions defined in Eq. (1) due to the estimated $\pm\sigma$ errors of the coefficients. The inset shows $\mathcal{D}_v^{\max}$ (normalized) and η (see text) as a function of mean storage times. The solid lines through the data points represent a fit to an exponential decay with $\tau = 240$ msec. The dashed lines marked ANL show the corresponding calculated values for the results of Ref. [4].

sions) tagged by the charge state of the carbon ion (either $q = +3$ or $q = +4$) and storage time before the Coulomb explosion. The storage times were registered between 10 msec and 4 sec. Selecting a storage time bin and a charge state, the list of the H-C-H angles in V space—θ_v—can be filed. The estimated angular resolution of the raw data for a single event is about 1° (see [1] for individual particle resolution).

The procedure of estimating the angular distribution $\mathcal{D}_v(x_v)$ ($x_v = \cos\theta_v$) from the data has been described in detail in Refs. [3] and [4]. Briefly, it is expanded in a set of smooth orthonormal functions $F_k(x_v)$:

$$\mathcal{D}_v(x_v) = \sum_k f_k F_k(x_v), \tag{1}$$

where the coefficients f_k are extracted from the raw data by

$$f_k = \sum_{n=1}^{N} F_k(x_v(n))/N \tag{2}$$

with $x_v(n)$ being the cosine, $\cos\theta_v$, of the nth event and the total number of measured events is denoted by N. The choice of the orthogonal basis F_k was such that the covariance matrix of the coefficients f_k was diagonal. At that stage, the number of functions $F_k(x_v)$ was reduced such that only significant f_k were used.

Equation (1) can be used for the evaluation of the experimental V-space distribution at any angle with its associated statistical error. Such angular distributions at different storage times are shown in Fig. 1 for the $q = +4$ data. The effects of the cooling are evident by observing the peaks of the distributions $\mathcal{D}_v^{\max}$ and the ratios $\eta = \mathcal{D}_v(-1)/\mathcal{D}_v^{\max}$ as a function of the mean storage time (inset in Fig. 1). Notice that η—the relative population at linearity—is significantly larger for shorter storage times. Results consistent with the above are observed for data coincident with the carbon $q = +3$ charge state.

As shown in Fig. 1, the cooling process can be well described by an exponential decay ($\tau = 240 \pm 20$ msec). Thus, for the bending degree of freedom it can be safely assumed that the events with storage time of 1–4 sec are close to room temperature.

The extraction of an R-space angular distribution $\mathcal{D}(x)$ as a function of $x = \cos\theta$, which is consistent with the best fit to the data, was carried out by the method introduced in Ref. [3] (see also Ref. [4]). For the coldest storage interval of 1–4 sec, the end result was a set of five statistically significant coefficients g_k and associated uncorrelated errors which define an angular distribution, $\mathcal{D}(x)$, through a linear combination of orthonormal functions $G_k(x)$,

$$\mathcal{D}(x) = \sum_{k=1}^{5} g_k G_k(x). \tag{3}$$

The coefficients for the two measured carbon ion charge states $q = +3$ and $q = +4$ and their associated errors were found to be statistically consistent with each other. The R-space angular distributions from data coincident with the two charge states are shown by the two almost overlapping lines in Fig. 2. This insensitivity of the final result to the charge state supports the basic and simple physical model which is used for simulating the CEI process [5]. The feature of the R-space density which is most important for further discussion is the finite density near the linear conformation, $\mathcal{D}(x = -1)$. We point out that this feature is inherent in the raw data (Fig. 1) and does not depend on the details of the R-space analysis.

One motivation for performing this experiment was to examine the supersonic expansion cooling method used for the CEI experiment of CH_2^+ at Argonne National Laboratory (ANL) [4,6] by comparing it with the radiative cooling method of the present study. Inspecting the two experimental R-space distributions, one finds that both are peaked at the same location and have significant density at linearity. Therefore it is reasonable to compare simulated $\mathcal{D}_v^{\max}$ and η from the older R-space results for the same experimental conditions of the reported study. These are shown by the horizontal dashed lines marked ANL in Fig. 1. Evidently, the new results at the 1–4 sec delay interval are substantially colder.

In previous CEI work, whenever cooling efforts were applied to reach the vibrational ground state, the measured nuclear configuration density function was compared with the square of the vibrational ground-state wave function which is a solution of the Born-Oppenheimer (BO) ground-state potential-energy surface. In cases where the Renner-Teller effect applies, the lower potential was used. We therefore start the comparison with theory along the same lines.

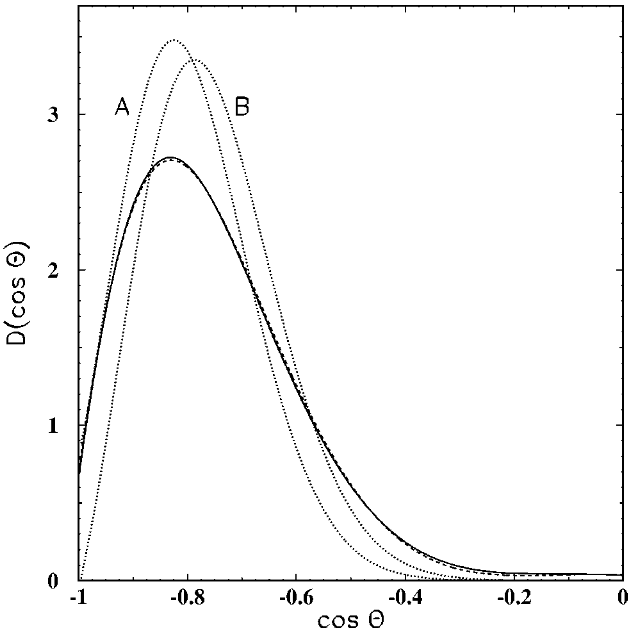

FIG. 2. Comparison of the CEI measurement to theories. The R-space bending angle analysis results of $1 \leqslant t_s \leqslant 4s$ data for the two carbon charge states are almost overlapping (full line for $q=+4$ and a dashed line for $q=+3$). The theoretical predictions are represented by dotted lines: (A) the square of the ground-state bending wave function within the BO approximation [7] and (B) the square of the ground-state bending wave function within the adiabatic approximation [7].

The most recent BO potential surface is given by Ref. [7]. The square of the ground-state bending wave function [8] in the BO potential from Ref. [7] is shown in Fig. 2 [dotted line (A)] together with the CEI experimental bending distribution of data in the 1–4 sec delay interval. The peak of the experimental distribution at $x_{\max}=-0.83$ (146°) fits well the peak of the theoretical curve at $x_{\mathrm{BO}}=-0.82$ (145°). The width of the new experimental results, though narrower than the older ANL measurement, is still significantly broader than the theory. As will be explained below, the above theoretical density is inconsistent with current theories on the structure of low-lying states of CH_2^+.

There is a vast amount of literature on theoretical aspects of quasilinear molecules and the Renner-Teller effect. Here, we mainly refer to the latest theoretical publication on CH_2^+ [7], where the reader can trace the many other references and different methods of treatment. The adiabatic approach starts with the BO states, specifically, at any nuclear conformation the lowest electronic eigenenergy and an associated electronic eigenstate are found. Generally, at linearity, different projections of the electronic angular momentum Λ have large energy spacing in comparison with vibrations and rotations spacings. For bent conformations correlated to $\Lambda \neq 0$ ($\Lambda=1$ for CH_2^+), the electronic eigenenergies are split by coupling to the nuclear rotations around the symmetry axis—the Renner-Teller effect. References [7] and [9] emphasize that the adiabatic potential which governs the nuclear dynamics contains not only the BO electronic energies but an additional energy term

$$A(R)=\frac{1}{2}\mu_{zz}(R)\hbar^2\Lambda^2, \tag{4}$$

where $\mu_{zz}(R)$ is the inverse of the smallest moment of inertia at the conformation R. This term diverges at linearity. Moreover, it is shown in Ref. [9] that for any general total angular momentum, the solution for the wave function near linearity is a superposition of terms $\propto(\pi-\theta)^{|K\pm\Lambda|+1/2}$, where K is an eigenvalue of $\mathbf{N_z}$ (the total angular momentum and the spin operators are $\mathbf{J}$, $\mathbf{S}$, respectively, and $\mathbf{N}=\mathbf{J}-\mathbf{S}$). Only a term with $|K\pm\Lambda|=0$ can contribute to the density $\mathcal{D}(\cos\theta)$ at linearity (see [8]). For ensembles at temperatures of 300 K or more, where there is small expectation for the lowest total angular momenta, such terms are suppressed by statistical arguments. The contribution of these terms to the density at higher excitations, where larger angular momenta play a role, should be even smaller due to the decrease in their statistical weight. Thus, the zero density at linearity should be even more pronounced at higher excitations, in contrast to the experimental findings.

In summary, the approximation which requires a single (double for Renner-Teller cases) potential-energy surface for the dynamics of nuclei in molecules predicts, in general, a zero density at linearity. The density should increase with a power law which critically depends on the total angular momentum quantum number. Thus, the comparison of CEI data to densities derived from a potential without the correction term [Eq. (4)] such as the one shown by the dotted line (A) in Fig. 2 is inconsistent with current adiabatic theories.

Adiabatic bending wave functions for CH_2^+ were calculated in Ref. [7] for $N=0$. The adiabatic ground-state bending density from Ref. [7] is shown in Fig. 2 as the dotted line (B). Notice that the peak of the cosine (angle) distribution is $x_{\mathrm{AD}}=-0.79$ (142°), which is appreciably higher than the experimental peak $x_{\max}=-0.83$ (146°). As discussed above, this density rises linearly from zero starting at $x=-1$. At about 300 K, the theoretical density should rise from zero with a power higher than 1. It should curve faster away from $x=-1$ than the density calculated for the $N=0$ case. Therefore, the highly significant finite density at $x=-1$ of the data reported here and shown in Fig. 2 cannot be explained by a hot statistical distribution of the adiabatic states. If we disregard possible, but unlikely, electronic isomeric states with lifetimes longer than a few seconds or an unusual population of $K=1$ states at 300 K, this is a clear indication of large nonadiabatic contributions to the low-lying states of CH_2^+. The systematic behavior of $\mathcal{D}_v(-1)$ with storage time (Fig. 1) is an additional strong support to the conclusion of large nonadiabatic contributions. It shows that the density at linearity is consistently higher for smaller storage times in spite of the larger angular momenta content at higher excitations. This piece of evidence is embedded in the raw V-space data and is independent of further analysis.

Conversely, nonadiabatic amplitudes should be highly sensitive to the excitation energy and must grow with increasing excitation of the ensemble. This is compatible with the observations. The divergence of $A(R)$ in Eq. (4) suggests the source of the nonadiabaticity to be due to an avoided crossing with an excited $\Lambda=0$ electronic state.

A rough estimate of the nonadiabatic fraction can be derived from the data assuming that (a) the measured ‘‘cold’’ R-space distribution represents the true bending density, (b) the calculated adiabatic ground-state density must be a part of the true density, and (c) after subtraction, the leftover nonadiabatic density must be a smooth positive function of the angle. This rough estimate results in more than 50% nonadiabatic contributions and even more for the hotter distributions.

The CEI results show clearly that a nonadiabatic extension of the existing CH_2^+ theories is needed for a correct description of the wave functions. The quasilinear example happens to be a favorable case because its adiabatic description forbids a finite density at linearity and the CEI is as sensitive to the linear conformation as to other conformations. Therefore such experiments serve as a direct measure of the applicability of the adiabatic approach for predicting molecular wave functions.

Examining Fig. 2, it is curious to find that the theoretical prediction based on the bare BO approximation fits the experimental findings so well. Moreover, the state-of-the-art adiabatic correction shifts the theory significantly away from the experiment: The most probable angle shifts substantially to smaller angles and, more importantly, the experimentally significant finite density at the vicinity of $\cos\theta=-1$ are not compatible with the theoretical prediction. The needed nonadiabatic terms in the wave functions are estimated to be quite large.

In conclusion, we have shown that experimentally significant findings on the density of H-C-H angles in the CH_2^+ ground state are in conflict with the standard Renner-Teller treatment of linear molecules. In particular, restricting the space of the electronic states to only the two lowest ones is inconsistent with the experimentally found significant finite density at the linear conformations.

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