

Angle-resolved photoelectron spectrum of rotational states in H_2^+

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We have recorded an angle-resolved photoelectron spectrum of the first four vibrational peaks of the $X^2\Sigma_g^+$ state of H_2^+ . In the spectrum, the individual peaks of the $\Delta N=0$ rotational branch are completely resolved. From curve fitting of the rotational branches, we found the anisotropy parameter of the $|\bar{\mu}(0,0)|^2$ squared reduced multipole moment matrix element to be $\beta=1.85$, with no significant difference between the vibrational states. For the $|\bar{\mu}(2,0)|^2$ squared reduced multipole moment matrix element, we found $\beta(\nu=0)=0.83$, decreasing slightly at higher vibrational levels. The earlier observed increase in the β parameter with vibrational quantum number is mainly explained by a decreased size of $|\bar{\mu}(2,0)|^2$ relative to $|\bar{\mu}(0,0)|^2$, dominating the β decrease of the $|\bar{\mu}(2,0)|^2$ squared reduced multipole moment matrix element itself. We have also determined the β value of individual peaks in the $\Delta N=0$ branch. The difference in β between the peaks in this branch is small. In particular, the 0-0 transition does not seem to have a considerably higher β value than the other members of the $\Delta N=0$ branch, which is expected from theory. [S1050-2947(98)12409-5]

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I. INTRODUCTION

Rotationally resolved photoelectron spectra can give interesting information about the photoionization process. Unfortunately, the rotational energy spacing is usually so small that the rotational levels cannot be resolved by conventional photoelectron spectroscopy (PES). The PES studies that have been done have mainly concerned hydrogen [1–5] and hydrogen halides [6,7]. With threshold and near-threshold techniques like zero-kinetic-energy pulsed-field ionization (ZEKE-PFI) and resonantly enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PES), the number of molecules possible to study has been considerably extended. In spite of this, there have not been many investigations of the photoelectron angular distribution of rotational states in molecules. With resonance lamp ionization, only the angular distribution of photoelectrons of H_2 has been studied. Niehaus and Ruf [2] studied the vibration $\nu=0$ at room temperature with Ne I photons ($\lambda=736 \text{ \AA}$), giving β values for both Q and S branches, i.e., the transitions where the difference in rotational quantum number excluding spin N is $\Delta N=0$ and 2, respectively. For the $\Delta N=0$ branch, β was expected to be close to 2, and this was what was found. For the $\Delta N=2$ branch, the β value was higher than what was expected for p partial waves, showing that higher-order partial waves were involved. Later experiments confirmed these facts. In order to reduce the number of populated rotational levels in the ground state, Pollard *et al.* [3] and Ruf, Bregel, and Hotop [4] used supersonically cooled H_2 , and studied it with both Ne and He I ($\lambda=584 \text{ \AA}$) radiation. In both papers, the β value of the S branch is given as a relative to theoretical values close to 2 for the Q branch. Takahashi *et al.* [5] also measured the β value of the S branch as a relative to a theoretical value for the Q branch for room-temperature H_2 , and only with Ne I radiation. In these resonance lamp studies, unpolarized light was used, and in none

of them were individual rotational peaks resolved, the energy resolution being 10 meV or more.

In the near threshold energy region, a few studies of the $X^1\Sigma^+$ state of NO^+ [8–13] have been performed with REMPI-PES. By selecting highly excited rotational states in the intermediate electronic state, the energy separation of the rotational states in the photoelectron spectrum will be comparatively large. Under this circumstance, the energy resolution has been sufficient to investigate the photoelectron angular anisotropy of individual rotational transitions. The kinetic energy of the photoelectrons were typically around 200 meV in these studies. Reiser, Rieger, and Müller-Dethlefs [14] studied the photoelectron angular anisotropy of the lowest rotational states of the same electronic state of NO^+ with a near-ZEKE technique, where the kinetic energy of the photoelectrons is of the order of tenths of a meV. The risk of distorting the angular distribution at this very low kinetic energy is obvious. The analyzer used in Ref. [14] had a large angular acceptance (29°), and could not definitely establish a value for the anisotropy parameter of the photoelectrons. Since the photoelectrons are very close to threshold in all these studies, a sensitivity to rotational and vibrational autoionization cannot be excluded. Such effects have been studied for H_2 at vibrational resolution by Dehmer *et al.* [15].

We have been able to record angle-resolved photoelectron spectra, excited with polarized He I radiation, with an energy resolution of 3 meV. This resolution has been sufficient to determine the photoelectron anisotropy parameter for individual rotational states in the $\Delta N=0$ branch of the $X^2\Sigma_g^+$ state of H_2^+ . This is the first time the β parameter for an individual rotational state, ionized with a single photon, has been determined. Since this is $\Sigma \rightarrow \Sigma$ transition, Hund's case (b) coupling applies in both initial and final state. We have used the model of Xie and Zare [16], which is valid for Hund's case (b), and determined the relative squared reduced multipole moment matrix elements by curve fitting the spectra, and compared these with earlier experimental results.

II. EXPERIMENT

The spectrometer used in the experiment was a truncated hemispherical analyzer with 144-mm mean radius [17,18]. The angle in the dispersive direction accepted into the analyzer was less than 20 mrad. In order to reduce the Doppler broadening, it has since the publication of Ref. [18] been fitted with an effusive beam source, with compensating electrodes for plasma potential gradients and work-function drifts in the ionizing region. The beam was created by passage through a multichannel plate with straight channels. The pressure on the reservoir side of the beam source was typically a few tenths of a mbar, so molecular flow conditions could be said to apply, thus the cooling effect of the beam was negligible. The He I radiation was generated with an electron cyclotron resonance (ECR) uv lamp, giving very intense light with a measured line width of 1.2 meV [19]. The light was polarized by a simple arrangement with two gold-plated mirrors. After the polarizer, the light was reflected in a grating monochromator which is ordinarily used for monochromatization of He II radiation. This was set for zero-order light, i.e., only reflecting, and polarized the light further. Light source, mirror arrangement, and monochromator swing around the ionization region on a rotating feedthrough. The size of the mirrors limited the light, giving it a rectangular cross section. When the angle between the major polarization axis and the acceptance of the spectrometer was changed from 0° to 90°, the size of the ionization volume seen by the spectrometer decreased. The intensity of the measured spectrum was then decreased by a geometrical factor. This factor had to be determined by measuring intensities of a substance with a known β parameter. The polarization also has to be determined experimentally. To do this, we measured the intensities of the outermost valence p orbitals of Ar, Kr and Xe, for which the β parameters are well known from literature [20,21]. Measuring two substances simultaneously is sufficient to obtain both the geometrical factor due to the rectangular shape of the ionization region, and the degree of polarization. This was done before and after the experiment. The degree of polarization was found to be $P = 0.92$, and not to deteriorate measurably during the time the experiment was conducted. The H_2 spectrum was obtained simultaneously with a spectrum of the $4p_{3/2}$ peak of Kr with the binding energy 13.9998 eV [22], to calibrate the energy and to check the geometrical factor. The sample gas was a 20%-80% mixture of Kr- H_2 . The H_2 gas was of 99.9999% purity, and the Kr gas of 99.998% purity, both commercially acquired. The recording lasted 36 h, alternating sweeps with 0° and 90° to the main direction of polarization.

III. RESULTS AND DISCUSSION

In Fig. 1 an overall spectrum is shown, both at 0° and at 90°. The 90° spectrum has first been scaled with the geometrical factor determined from the Kr peak, and then multiplied by a factor to facilitate a comparison with the 0° spectrum. In the spectrum, we observe peaks for transitions with the change in rotational quantum number $\Delta N = 0, \pm 2$. Odd changes in rotational quantum number are not allowed [23], and $\Delta N = \pm 4$ and higher have intensities too low to

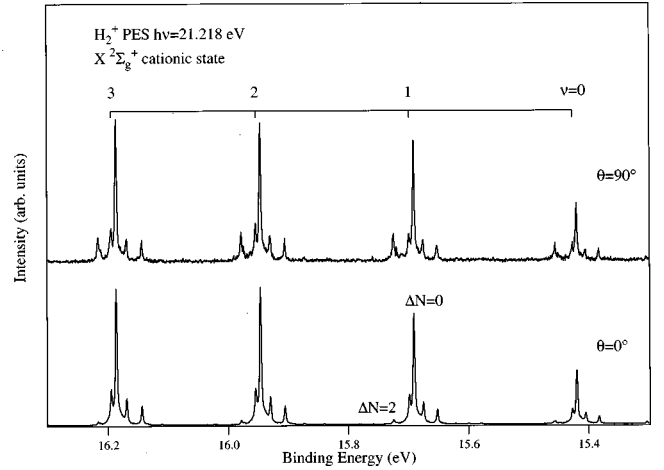


FIG. 1. He I excited spectrum of the four first vibrational peaks in the $X \ 2\Sigma_g^+$ state of H_2^+ , recorded with $\theta = 90^\circ$ (top, scaled to facilitate comparison) and $\theta = 0^\circ$ (bottom). The $\Delta N = 0$ and 2 branches are indicated for the $\nu = 1$ vibration with $\theta = 0^\circ$. The individual states of the $\Delta N = 0$ branch are completely resolved. Note in particular the large difference in intensity between the $\theta = 0^\circ$ and 90° spectra for the $\Delta N = 0$ and 2 branches.

show up in the spectra. The spectra can be considered to be free of disturbing satellites, except for an overlap between the $\Delta N = 2$ branch of $\nu = 0$ and the $\Delta N = 0$ branch of the He I β ionized vibration $\nu = 9$. The energies of the resolved rotational states match those calculated in Ref. [24] to within 0.2 meV. It is immediately clear from the spectra that the $\Delta N = 2$ branch has a much lower β value than $\Delta N = 0$ branch. Another thing that is clear is that the β value of the $\Delta N = 0$ branch is very high. This is also the result of the He I studies in Refs. [3] and [4]. Noteworthy is the fact that the 0-0 transition of the $\Delta N = 0$ branch does not seem to have a β value much different from the rest of the members in the $\Delta N = 0$ branch.

The spectrum has been curve fitted to obtain the squared reduced multipole moment matrix elements for the $1\Sigma_g^+ \rightarrow 2\Sigma_g^+$ transition. In the curve-fitting procedure, the energy position of the rotational peaks was calculated as

$$E_{b(\nu, N, N^+)} = E_{b(\nu, 0, 0)} + B_\nu^+ N^+ (N^+ + 1) - D_\nu^+ [N^+ (N^+ + 1)]^2 - BN(N+1) + D[N(N+1)]^2, \quad (1)$$

where B_ν^+ and D_ν^+ are the rotational constants of the vibration ν in the ionic state, and B and D refer to the initial state. Literature values were used for B and D [25], but for the

TABLE I. Measured rotational constants in units of cm^{-1} of the first four vibrations in the $X \ 2\Sigma_g^+$ state of H_2^+ , compared with the values given by Pollard *et al.* [26].

ν	B_ν This work	D_ν This work	B_ν Ref. [26]	D_ν Ref. [26]
0	30.1	0.09	29.6 ± 2.5	0.03 ± 0.08
1	28.1	0.06	28.1 ± 1.1	0.04 ± 0.04
2	26.4	0.03	26.4 ± 1.1	0.03 ± 0.03
3	24.8	0.03	24.8 ± 0.5	0.02 ± 0.02

ionic state rotational constants had to be found from the spectra. The values found from our spectra are presented in Table I, and are very similar to those given by Pollard *et al.* [26].

The intensities of the rotational lines were calculated according to the model of Xie and Zare [16]. With the angular anisotropy of single-photon ionization explicitly included, the line strength is given by

$$I(N, N^+, \theta, \nu) = [2 - (-1)^N] \exp\left(-\frac{BN(N+1) - D[N(N+1)]^2}{kT}\right) (2N+1)(2N^++1) \left[\frac{\delta_{NN^+}}{(2N+1)} |\bar{\mu}_\nu(0,0)|^2\right. \\ \left. \times \left(1 + \frac{\beta_{0\nu}}{4}(3P \cos 2\theta + 1)\right) + \begin{pmatrix} N & 2 & N^+ \\ 0 & 0 & 0 \end{pmatrix}^2 |\bar{\mu}_\nu(2,0)|^2 \left(1 + \frac{\beta_{2\nu}}{4}(3P \cos 2\theta + 1)\right)\right], \quad (2)$$

where $|\bar{\mu}_\nu(k,0)|^2$ are the squared reduced multipole moment matrix elements for vibration ν and angular momentum k , θ is the photoelectron ejection angle to the major polarization axis, $\beta_{k\nu}$ is the photoelectron anisotropy parameter for $|\bar{\mu}_\nu(k,0)|^2$, and P is the degree of polarization of the incident radiation. In the rest of this paper, the subscript ν will be dropped from squared reduced multipole moment matrix elements, and photoelectron anisotropy parameter. Only rotational branches with $\Delta N = N^+ - N = 0, \pm 2$ have non-negligible intensity, and this means that the intensity can be described by the two parameters $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(2,0)|^2$ [16]. The squared reduced multipole moment matrix element $|\bar{\mu}(0,0)|^2$ will only affect the intensity of the $\Delta N = 0$ branch, whereas $|\bar{\mu}(2,0)|^2$ will affect $\Delta N = 0$ and ± 2 branches. This coupling of the intensity of the rotational branches, squared

reduced multipole moment matrix elements and anisotropy parameters makes the error estimation very difficult, and we have abstained from giving error limits. The factor $2 - (-1)^N$ is to account for the nuclear-spin degeneration of the ground-state rotational population in H_2 . The sample was at room temperature during the experiment.

Each line was broadened with two Gaussians, one which is only spectrometer broadened, corresponding to the highly directed effusive molecular beam, and another part corresponding to scattered molecules, that is both Doppler and spectrometer broadened. The spectrometer function and the ratio of the Doppler to non-Doppler broadened parts is usually found by fitting a combination of the two parts to the energy calibration line. However, the ratio was mostly determined by the compression of the pump used at the ionizing region, and this differed dramatically for H_2 and Kr for the turbo pump we used. We therefore determined the Doppler to non-Doppler ratio by fitting the H_2 peaks themselves. An example of a fit obtained with the outlined method is presented in Fig. 2. For each vibration, a least-square fit was made for $\theta = 0^\circ$ and 90° . The intensities were then corrected for the geometrical factor, as mentioned above, and the relative size and the angular anisotropy parameter was determined for each squared reduced multipole moment matrix element.

Results for the four vibrations are presented in Table II

TABLE II. Measured anisotropy parameter and relative size of $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(2,0)|^2$ for the first four vibrations in the $X^2\Sigma_g^+$ state of H_2^+ , excited with He I radiation. The β values for $k=0$ for both Refs. [3] and [4] actually refers to the Q branch, and are theoretical values used to derive the β value of the S branch, which are given in the row for $k=2$. The β value for $|\bar{\mu}(2,0)|^2$ is equivalent to the β value of the S branch, but the Q branch β value differs slightly from the $|\bar{\mu}(0,0)|^2\beta$ value. A vibrationally averaged β value is also given.

	$ \bar{\mu}(k,0) ^2$	β_k , this work	β , Ref. [3]	β , Ref. [4]
$\nu=0$		1.73		
$k=0$	1.000	1.86	1.9 ± 0.1	1.918
$k=2$	0.141	0.83	0.87(19)	0.81(17)
$\nu=1$		1.74		
$k=0$	1.000	1.86		1.932
$k=2$	0.106	0.63		0.71(16)
$\nu=2$		1.75		
$k=0$	1.000	1.85		1.942
$k=2$	0.083	0.59		0.73(15)
$\nu=3$		1.76		
$k=0$	1.000	1.85		1.949
$k=2$	0.069	0.47		0.80(16)

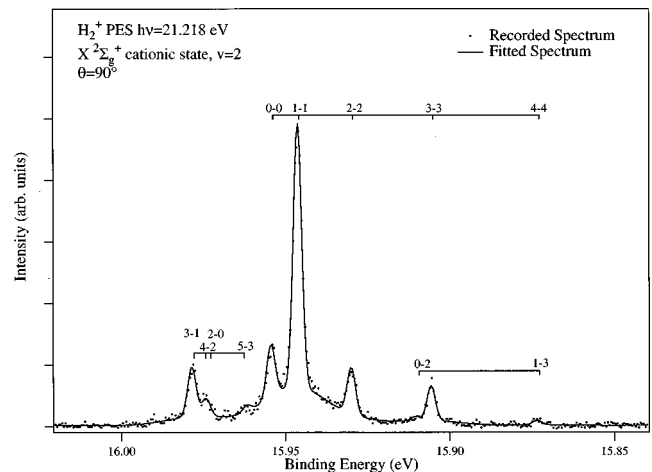


FIG. 2. A least square fit of the $\nu=2$ peak of $X^2\Sigma_g^+$ state of H_2^+ , recorded at $\theta=90^\circ$ (experimental, dotted line, fit, solid line).

TABLE III. Measured and calculated angular anisotropy parameter and intensity compared to the 1-1 transition for rotational states in the $\Delta N=0$ branch of the first four vibrations in the $X^2\Sigma_g^+$ state of H_2^+ . The intensities for Itikawa [27] taken from Ref. [16] for $\nu=0$, and calculated from values in the original paper for $\nu=2$. The numbers in parentheses indicate the errors.

State	β , this work	β , Ref. [27]	Intensity, this work	Intensity, Ref. [27]
$\nu=0$				
0-0	1.79(9)	2.0	0.21(6)	0.185
1-1	1.79(5)	1.871	1.00(3)	1.000
2-2	1.85(8)	1.906	0.18(6)	0.175
3-3	1.68(11)	1.912	0.15(6)	0.133
$\nu=1$				
0-0	1.85(7)		0.19(6)	
1-1	1.79(5)		1.00(3)	
2-2	1.85(7)		0.17(6)	
3-3	1.78(7)		0.14(6)	
$\nu=2$				
0-0	1.80(7)	2.0	0.20(6)	0.191
1-1	1.80(5)	1.922	1.00(3)	1.000
2-2	1.82(7)	1.943	0.18(6)	0.176
3-3	1.78(7)	1.931	0.14(6)	0.134
$\nu=3$				
0-0	1.82(7)		0.19(6)	
1-1	1.80(5)		1.00(3)	
2-2	1.88(6)		0.18(5)	
3-3	1.79(7)		0.14(6)	

together with some earlier experimental results. The β value of $|\bar{\mu}(0,0)|^2$ is compared to values for the $\Delta N=0$ branch, and these are not immediately comparable, since $|\bar{\mu}(2,0)|^2$ and β_2 also affects the intensity of the $\Delta N=0$ branch. However, these values are theoretical for both Refs. [4] and [3], and the effect of the $|\bar{\mu}(2,0)|^2$ squared reduced multipole moment matrix element is rather small. The value β_2 for $|\bar{\mu}(2,0)|^2$ is compared to β value of the $\Delta N=2$ branch, and these are equivalent. In the same table, the relative size of the squared reduced multipole moment matrix element and the anisotropy parameter for the vibrations as a total are also presented.

The β value for $|\bar{\mu}(0,0)|^2$ is approximately 1.85 for all for four vibrations. For $|\bar{\mu}(2,0)|^2$ much lower values were obtained, varying from $\beta_2=0.83$ for $\nu=0$ to $\beta_2=0.47$ for $\nu=3$. Considering the fact that we get a change in the size of the ionizing region when changing the angle, and have to rely on calibration by rare-gas lines to obtain the true intensity, we may have a minor systematic error in our measurements. The relative intensity variations, on the other hand, should be reliable, so the large difference in β value for $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(2,0)|^2$ branches is certainly a valid observation. Our results for the $|\bar{\mu}(2,0)|^2$ branch or equivalently the $\Delta N=2$ branch, essentially agree with earlier experiments [3,4]. Since the photoelectron is ejected from a σ orbital, and has relatively low kinetic energy, it is expected to have mainly p -wave character, but the β value of $\Delta N=2$ branch

is higher than what is expected for pure p waves. Calculations where higher partial waves have been included in the description of the photoionization process [27–29] are in better agreement with experiment. The slight increase in β value for the vibrations in total with higher vibrational quantum number is seen to depend primarily upon a decrease in the relative size of the $|\bar{\mu}(2,0)|^2$ squared reduced multipole moment matrix element. Actually, the β value of $|\bar{\mu}(2,0)|^2$ decreases with higher vibrational quantum numbers. Ruf, Bregel, and Hotop [4] also measured a decreased branching ratio of the $\Delta N=2$ branch, but their β value showed no definite trend. The decrease in both the β value and the relative size of $|\bar{\mu}(2,0)|^2$ is in qualitative agreement with calculations by Itikawa [27] and Hara and Ogata [28]. For the vibrations in total, we obtain β values that are in good agreement with Poliakoff *et al.* [30], but slightly lower than those given by Kreile and Schweig [20].

We have also determined the β value for individual rotational states in the $\Delta N=0$ branch. The intensities of the 0-0, 1-1, 2-2, and 3-3 peaks at $\theta=0^\circ$ and 0° were determined from the spectra presented in Fig. 1. Each peak was fitted with the two Gaussians mentioned above, corresponding to the effusive beam and to scattered molecules. The relative intensities and β values of the individual rotational states are presented in Table III. As seen there, the anisotropy parameter does not vary markedly within the rotational branch or between vibrations. The 0-0 transitions should really be completely determined by $|\bar{\mu}(0,0)|^2$, and the corresponding

peaks could be expected to have the same β value as $|\bar{\mu}(0,0)|^2$. However, the values for the squared reduced multipole moment matrix elements were determined from least-square fits of the whole rotational branches, and need not give the same result. In fact, the intense 1-1 transition can be expected to determine $|\bar{\mu}(0,0)|^2$ to a large extent.

When the total angular momentum excluding spin, i.e., the sum of rotational and orbital angular momentum, is zero in both initial and final states, the outgoing photoelectron is expected to carry all of the angular momentum of the ionizing photon without interacting with the ionic core, and hence be a pure p wave with $\beta=2$. In this study, both initial and final states are Σ states, so for the 0-0 transition, and equivalently $|\bar{\mu}(0,0)|^2$, the β value is expected to be 2. For other members of the $\Delta N=0$ branch, this does not apply. Itikawa [27] and Dill [31] suggested that the β value of the N - N transitions other than 0-0 should be considerably lower than 2. This does not agree with our measurements. The differences between the rotational states that we can see tend to be small, and if anything, the 0-0 transition seems to have a lower β value than, for instance, the 2-2 transition, which is of approximately the same intensity. Even though our calibration could give rise to a minor absolute error, the relative intensities are obtained with precision. Chandra [29], using more advanced methods of calculation, obtained differences in β between the individual rotational states that are smaller than what was suggested by Itikawa [27] and Dill [31]. In general our measurements give β values of the individual rotational states that are lower than what theory predicts. In particular, it is unlikely that the 0-0 transition could have a β value as high as 2. The intensity ratio between the 0° and 90° spectra is around 13 for all peaks in the $\Delta N=0$ branch, and this ratio has to be 50% larger to encompass the value $\beta=2$ within error bars. Even though the absolute value of β may be affected by the calibration procedure, such a large error is hardly possible. This surprisingly low value for the anisotropy parameter of the 0-0 transition could possibly be due to some unknown near threshold effect, even though the photoelectrons have a kinetic energy of around 5 eV.

The relative intensity of the peaks within the $\Delta N=0$ branch is well described theoretically, being mainly given by

the Boltzmann distribution and the nuclear spin degeneration. For the $\Delta N=2$ branch, some of the individual rotational states are resolved, but, due to the overlap of the Doppler tails of the $\Delta N=0$ branch and the low intensity, we have only attempted to analyze them as a group.

IV. CONCLUSION

In conclusion, we have recorded an angle-resolved spectrum of the four first vibrational peaks of the $X^2\Sigma_g^+$ state of H_2^+ , with sufficient energy resolution to clearly observe individual rotational states. Three rotational branches could be observed: the strong $\Delta N=0$ branch and the much weaker $\Delta N=\pm 2$ branches. The fact that transitions with $\Delta N\geq 4$ have too low an intensity to be seen in the spectrum means that only two squared reduced multipole moment matrix elements, $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(2,0)|^2$, have non-negligible sizes. From curve fitting of the rotational branches, the photoelectron anisotropy parameter and relative sizes of the squared reduced multipole moment matrix elements were determined. From these data, we found that the increase in β value with vibrational quantum number that has been observed for vibrations in the $X^2\Sigma_g^+$ state is due to a decrease in the relative size of $|\bar{\mu}(2,0)|^2$, which has a much lower β value than $|\bar{\mu}(0,0)|^2$. Actually, the β value of $|\bar{\mu}(0,0)|^2$ decreases with vibrational quantum number, but the decrease in size dominates over this effect.

We have also investigated the anisotropy parameter of individual states in the $\Delta N=0$ branch. We found only small differences in β value between peaks in this branch, and also between the vibrations studied. The β values were lower than what was expected from theory. Admittedly, our β values may suffer from a minor systematic error, but we believe that the discrepancy between experiment and theory is too large to be explained by this.

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