

Vibrational and rotational structure in the He I-excited photoelectron spectrum of the $A^2\Sigma_{1/2}^+$ state of HBr^+

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The $A^2\Sigma_{1/2}^+$ state of HBr^+ has been studied experimentally using He I photoelectron spectroscopy and theoretically employing an *ab initio* multireference configuration-interaction method. Vibrational structure has been observed throughout the band up to the dissociation limit. The vibrational lines corresponding to $v=3-9$ are much broadened due to strong interaction with repulsive states as found in earlier studies. In recordings with a resolution of about 4–5 meV, rotational structure has been observed for the $v=0, 1, 2, 11, 12,$ and 13 vibrational states. The spectra have been fitted using calculated rotational constants. It is found that the $\Delta N=\pm 1$ branches dominate the photoelectron bands but also the $\Delta N=\pm 3$ transitions are significant. For the lowest states the T branch ($\Delta N=3$) forms a well-separated band.

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I. INTRODUCTION

The $A^2\Sigma^+$ state of HBr^+ has been the subject of many experimental and theoretical studies with special attention to the vibrational and rotational structure. The state has been found to be strongly perturbed by interaction with three different repulsive electronic states of $^4\Pi, ^4\Sigma^-, ^2\Sigma^-$ symmetry [1–3]. Crossings between the potential curves are predicted between the $v=3$ and 5 vibrational levels of the $A^2\Sigma^+$ state and in this energy region fast predissociation of the cation is expected to take place [1]. In fact, the calculations by Banichevich, Klotz, and Peyerimhoff [1] suggest that only the $v=0$ and 1 levels are stable, which is in excellent agreement with $A^2\Sigma^+ \rightarrow X^2\Pi$ optical emission spectra exhibiting transitions from the $v=0$ and 1 vibrational states only [4,5]. A loss of rotational structure at $N=21$ of the $v=0$ level and at $N=12$ of the $v=1$ level is probably also related to this instability of the cation. The $v=2$ level has an energy of 15.609 eV and is therefore situated above the dissociation limit 15.572 eV of the perturbing states. This implies that the lifetime of the $v=2$ level is controlled by a potential barrier formed by the $A^2\Sigma^+$ state and the repulsive states and that tunneling through the barrier is faster than the time for optical transitions to the $X^2\Pi_{1/2}$ state. The calculated lifetime for the $v=2$ state is 1.52×10^{-10} s [1].

For the higher vibrational states ($v \geq 4$), lifetimes have been predicted to be very short, on the order of 10^{-14} s. Such short lifetimes lead to substantial state broadenings as have been observed both in photoelectron [2, 6–8] and Penning ionization spectra [2]. The influences on these spectra are dramatic; the vibrational spacings become irregular and the linewidths increase remarkably from the $v=4$ vibrational level [2, 6–9]. Yench, Ruf, and Hotop [2] obtained in their He I-excited photoelectron spectrum linewidths (full width at half maximum) of 28 meV

for the first few lines whereas for the $v=4$ line the width was found to increase to 130 meV. This line broadening also causes some diffuseness in the spectrum but, nevertheless, the progression could in their study be clearly followed up to $v=10$ or even 12 .

The width of the $v=3$ level was predicted to be 1.53×10^{-13} s [1]. Even the state broadening associated with this lifetime should be observable in photoelectron spectra and in Ref. [2] a linewidth of 38 meV was observed.

The calculations of Ref. [1] were performed for levels up to $v=9$, for which a lifetime of 2.91×10^{-14} s was obtained. This is only slightly larger than the lifetimes obtained for the $v=4-8$ levels and even smaller than the value obtained for the $v=6$ level, which may suggest that the lifetime above $v=3$ is generally in the 10^{-14} s range. In order to further study this and other questions related to this state experimentally we have carried out measurements at a resolution of about 5 meV or better.

In the determination of lifetimes from photoelectron spectra and comparisons with calculated results, rotationally resolved spectra are preferable in general. Otherwise, if the linewidth has to be determined from rotationally averaged lines, the different rotational branches may give unpredictable broadenings that make the results uncertain. In the present investigation, rotational structure has been resolved both below and above the region of the potential curve crossings which makes possible rather detailed comparisons with the theoretical data. To support the analysis of the experimental data, and to be able to make curve fittings using proper rotational constants, we have calculated a potential curve along with the vibrational energies and the rotational constant B_v for the $A^2\Sigma^+$ state. This was done by means of the complete active-space self-consistent-field (CASSCF) [10] and multireference configuration-interaction (MRCI) [11] methods.

II. EXPERIMENTAL DETAILS

The studies have been performed by a photoelectron spectrometer described earlier in Ref. [12] and recently modified to considerably better performance utilizing the new high-resolution recording scheme reported in Ref. [13]. The highest energy resolution used in this study was about 4 meV. The He radiation was generated by a commercially available electron cyclotron resonance (ECR) uv source [14] giving a narrow linewidth and high brilliance. The HBr sample gas was of 99% purity commercially obtained. The gas was originally heavily contaminated with hydrogen, producing interfering lines in the region of interest (see Acknowledgments). This contamination could, however, be reduced to an insignificant level by cooling the gas container with liquid nitrogen followed by half an hour of pumping. It should be observed that the sample gas has to be transferred to a separate low-pressure reservoir prior to this distillation process.

The calibration and line-shape control of the spectrum was done using the Kr $4p_{3/2}$ line at 14.000 eV as energy reference. By this procedure, the accuracy in the position of well-defined peaks is $\pm 1-2$ meV.

All spectra are presented as they have been obtained from the spectrometer without any deconvolution or background subtraction. Rotational structure has been observed in many lines and in order to make a detailed analysis, curve fittings have been made. Gaussian lines have been used whenever appropriate. For the lifetime broadened lines good agreement with the experimental results was obtained only when using Lorentzian lines. From these fittings the line positions, widths, and relative intensities presented in the tables have been obtained. The fittings were carried out using a spreadsheet program (Excel), which was run on a Macintosh Quadra 700 computer in collaboration with Apple Computer AB in Sweden.

III. COMPUTATIONAL DETAILS

The basis set for bromine was taken from Ref. [15] and augmented with two d -type functions and one f -type function. The most diffuse s -type Rydberg function was not included. The basis set was contracted to $[10s8p4d1f]$. For hydrogen the contracted $[4s3p1d]$ basis set [16] was used. The core and inner valence orbit-

als, $1-7\sigma$ and $1-3\pi$, were treated as inactive in the CASSCF calculation. The 8σ , 9σ , 10σ , 11σ , 4π , and 5π orbitals were selected as active orbitals. With seven active electrons this gave 616 configurations in a CASSCF expansion in C_{2v} symmetry. The CAS calculations were followed by MRCI calculations. As a first step, primarily in order to obtain accurate results quickly, the reference states were selected by using a selection threshold of 0.05. This gave 11 configurations. Later on, the MRCI calculations were repeated with all configurations from the CASSCF included as reference states, a procedure sometimes referred to as second order CI. The $A^2\Sigma^+$ potential was calculated at 16 internuclear distances between 1.9 and 50 a.u.

IV. RESULTS

A. The full spectrum

The overall spectrum obtained in the present study is shown in Fig. 1. It exhibits a vibrational progression that can be clearly followed up to $v=14$ at 16.94 eV. Probably, also the $v=15$ line is observed at 16.97 eV, as will be discussed below. Structures can be seen even above the dissociation limit, but the interpretation of these is uncertain. The energies (peak maxima) and relative intensities obtained from this spectrum for the lines associated with the A state are summarized in Table I. Above $v=2$ the overlap between the lines is substantial. The relative intensities given for this range should therefore be considered approximate.

The vibrational energy levels expected in an unperturbed $A^2\Sigma^+$ potential were obtained theoretically by solving the Schrödinger equation numerically [17]. The result is given along with the experimental values in Table I. The agreement with the experimental data is good, but some comments may be made regarding the more detailed behavior. In the beginning of the band, the calculated spacings increase gradually compared to the experimental data. Good agreement between the theoretical and experimental data would not be expected in the $v=4-8$ region, so the cases of coincidence between theoretical and experimental results are fortuitous. Above 16.6 eV the calculated results are systematically lower than the experimental data. This reflects a

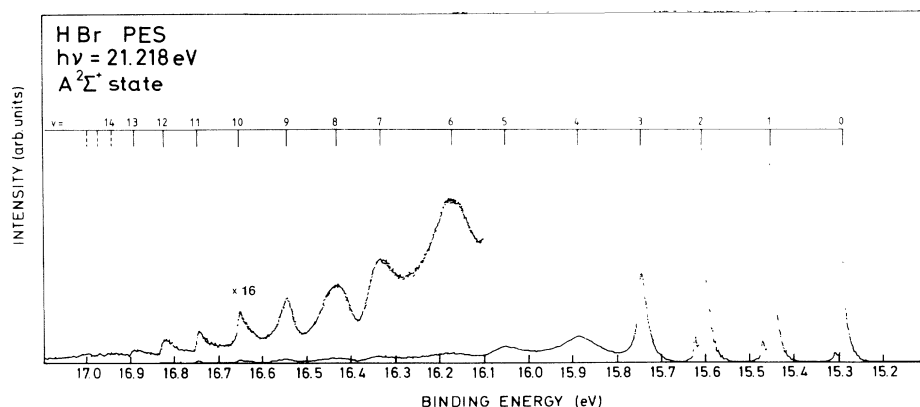


FIG. 1. The He I-excited photoelectron spectrum showing the $A^2\Sigma^+$ state of HBr^+ . The vibrational progression is indicated above the spectrum.

TABLE I. Observed and calculated energies and intensities for the vibrational levels of the $A^2\Sigma^+$ state of HBr^+ referred to $v=0$ of the neutral ground state. The intensity is normalized to 1 for the most intense line. The last column shows the rotational constant B_v calculated in the present study.

Vibrational quantum number v	$E_{\text{vib}}(\text{expt})$ (eV)	$E_{\text{vib}}(\text{calc})$ (eV)	$E_{\text{vib}}(\text{expt} - \text{calc})$ (meV)	Intensity	B_v (meV) (see text)
0	15.290	15.290	0	0.40	0.7498
1	15.454	15.462	-8.3	0.80	0.7177
2	15.608	15.625	-17	1.00	0.6859
3	15.744	15.779	-35	0.88	0.6550
4	15.885	15.924	-39	0.84	0.6249
5	16.050	16.061	-11	0.56	0.5956
6	16.176	16.180	4	0.36	0.5660
7	16.330	16.310	20	0.18	0.5360
8	16.430	16.403	27	0.11	0.5040
9	16.544	16.522	22	0.076	0.4720
10	16.649	16.615	34	0.036	0.4397
11	16.742	16.697	45	0.034	0.4053
12	16.821	16.770	51	0.018	0.3678
13	16.889	16.832	57	0.0084	0.3227
14	16.944	16.856	88	0.0052	
15	16.968	16.865	103		

deficiency of the *ab initio* method in predicting correctly the behavior of the potential curve near the dissociation limit.

B. Detailed line studies

The lines corresponding to $v=0-2$, observed in the 15.2–15.7 eV energy range, show a complex fine structure that can be associated with various rotational branches and also transitions between individual rotational levels of the initial and final states. The most striking features observed are a very asymmetric main line with a sharp edge on the high-binding-energy side and a tail extending far out on the low-binding-energy side. In addition, a weaker structure can be seen on the high-binding-energy side, shifted by about 15 meV from the main peak. This line shape is expected for ionization from a strongly bonding orbital, leading to a large increase in equilibrium bond distance. The sharp edge

reflects a band head, while the separate weak feature corresponds to a high-energy rotational branch.

Figure 2 shows a high-resolution recording of the $v=0$ line. Included in the figure are the energies of the P and N rotational branches. These were obtained using the rotational constants of Ref. [18] and the 0-0 point of the curve fittings (see below) to set the energy scale. These energies correspond well to the observed line structure in the experimental spectrum, which justifies an interpretation of the spectral lines in terms of rotational excitations. For the other branches that contribute substantially to the intensity, the spacings are too small for resolution of the rotational lines. The energy ranges of these branches are indicated in the figure. As can be seen, both the T ($\Delta N=3$) and U ($\Delta N=4$) branches are present in the spectrum. The former branch gives rise to the very characteristic peak observed on the high-binding-energy side of the main peak in the overall spectrum of Fig. 1. The S branch is apparently very weak.

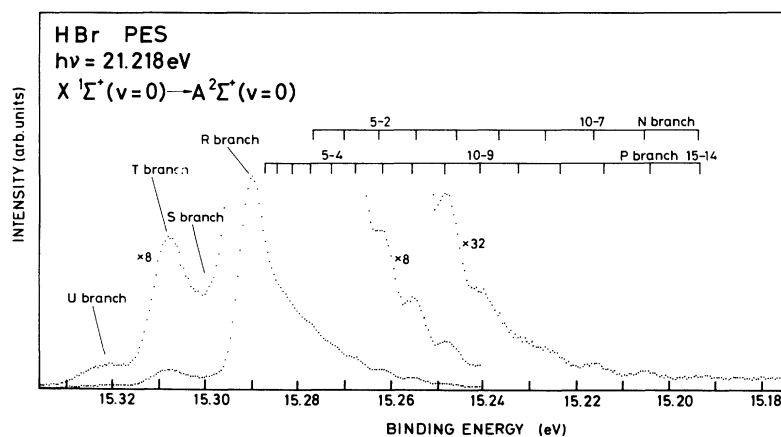


FIG. 2. A high-resolution recording of the $A^2\Sigma^+$ ($v=0$) state of HBr^+ . The positions of the rotational branches are indicated by arrows. For the P branch individual rotational lines can be seen. The calculated positions for these (see text) are indicated by the bar diagram. The intensity of the B branch is too low to contribute significantly to the structure.

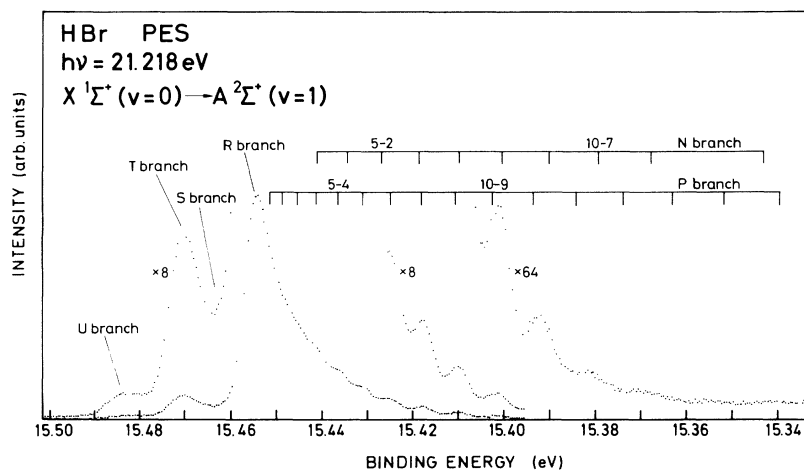


FIG. 3. A high-resolution recording of the line involving transitions to the $A^2\Sigma^+$ ($v=1$) state of HBr^+ .

Figure 3 shows a high-resolution recording of the $v=1$ line. It is similar to the $v=0$ line and the P and N branches that are drawn into the figure in a similar manner as in Fig. 2 explain the main features of the rotational structure.

Figure 4 shows a high-resolution recording of the $v=2$ line. It is similar to the $v=0$ and 1 lines and the P and N branches explain very well the rotational structure. It is noteworthy that the rotational structure of this state has not been observed in photon emission spectra, which suggests that predissociation is a much more likely decay channel than photon emission for this state. Since a line broadening cannot be observed in the present spectrum, the lifetime must be larger than at least about 10^{-13} s. In fact, the predicted lifetime is much larger, 1.52×10^{-10} s, as mentioned in the Introduction. The rotational structure can be followed at least to the $N=12$ state in the cation which has an energy of 93 meV. This is only about 47 meV below the $N=0$ level of the $v=3$ state.

The lines corresponding to $v=3-9$ are broad and lack the rotational fine structure observed in the lower lines. We therefore do not show them on separate figures. However, we will return to two of these lines below in connection with the curve fittings.

Figure 5 shows the lines from $v=11$ up to the dissocia-

tion limit. The lines corresponding to $v=11-13$, and also $v=10$, possess a profile that is similar to the first vibrational lines, i.e., a sharp edge on the high-binding-energy side and an extensive tail on the low-binding-energy side. In addition, the first three of these lines contain a remarkable fine structure that can be associated with the P and N rotational branches, as for the lowest vibrational lines. The calculated energies are indicated in the figure and, as can be seen, the agreement is very good. The vibrational lines gradually develop an almost triangular shape while the high-binding-energy edge gets somewhat rounded as the vibrational quantum number increases. Presumably, this reflects the fact that when the rotational levels become very close in energy near the dissociation limit, both the energy and intensity distributions in the transitions are determined essentially by the distribution of the initial state. For the line associated with $v=14$, the rotational structure can no longer be resolved, but a doublet structure is seen. The identification of the $v=15$ line is uncertain. Probably, the feature indicated by the bar is only a part of a more extended structure as in the case of the former line.

The vibrational bar diagram is terminated at 17.019 eV, which is the dissociation limit for the $A^2\Sigma^+$ state that corresponds to a separation into $\text{H} + \text{Br}^+(^1D)$. This

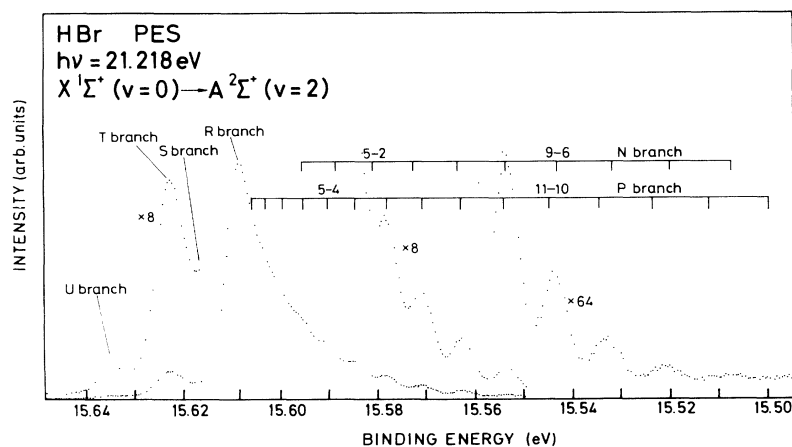


FIG. 4. A high-resolution recording showing the $A^2\Sigma^+$ ($v=2$) state of HBr^+ .

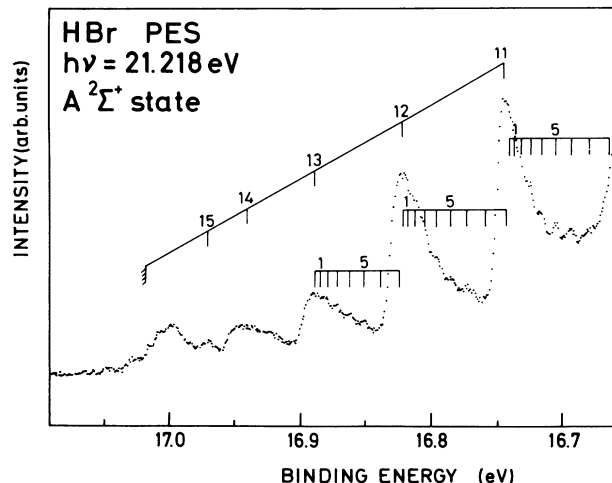


FIG. 5. The $A^2\Sigma^+$ ($v=11-13$) lines showing rotational structure corresponding essentially to the P branch. The expected positions for this branch are indicated above the spectrum.

energy was derived as the sum of the dissociation energy $D_0 = 3.758$ eV of the neutral ground state [18], the ionization energy of the Br atom (11.8468 eV), and the $^3P \rightarrow ^1D$ excitation energy (1.4145 eV) [19]. As can be seen, this energy corresponds well to the energy where the vibrational structure disappears, although some weak features can be seen in the 17.02–17.05 eV range.

C. Curve fittings

In order to quantify the observations regarding the rotational excitations, we have carried out curve fitting calculations for each vibrational line, as mentioned in Sec. II. In this procedure, the experimental curve was fitted by a sum of lines, each representing an individual rotational transition. Energies of the simple rotator were employed, and the relative intensities of the different rotational branches, as well as the zero point of the energy scale, were used as fitting parameters. The rotational energies were calculated using the rotational constant (B_v), which depends on the vibrational quantum number v . B_v

is related to B_e and the rotational constant α_e via the formula [20]

$$B_v = B_e - \alpha_e(v + \frac{1}{2}).$$

The intensity of each rotational transition was assumed to be determined by the population of the initial-state rotational level derived from a Boltzmann distribution and each rotational transition was represented by a Gaussian line.

Values of B_e and α_e used for determination of B_v for the $v=0$ and 1 states were taken from Ref. [18]. For level with $v \geq 2$ we have used values of B_v that were calculated using the *ab initio* potential curve. The results are listed in Table I. However, the calculated values are slightly too high, as can be seen from a comparison with the data of Ref. [18] and also the experimental results, and were therefore reduced by 5% in the energy calculations.

The parameters which gave the best fitting of the observed lines are collected in Table II, along with the rotational line width obtained in the curve fittings. In the fitting procedure, the set of parameters was obtained initially for each of the $v=0-2$ levels and could then be used with small modifications in the fitting of the lines $v=3$ and 11. However, in the case of the $v=3$ line it was necessary to use Lorentzians for the individual rotational lines. Although this line is rather weakly broadened, it was impossible to make a reasonable fit using Gaussians; either the wings were lacking or the width was too large near the top of the line. The rotational width for both $v=3$ and 4 was derived by successively broadening the lines in the fitting procedure until good agreement with the spectrum was obtained. No fittings were attempted for the lines $v=5-9$.

In the case of the $v=3$ line, the lifetime broadening is of the same order of magnitude as the spectrometer broadening obtained from the lower peaks. The most appropriate line for fittings should therefore be a Voigt function but this was not attempted due to the overlap with the $v=4$ line. However, even with Lorentzians a significant part of the intensity on the high-binding-energy side remains unexplained after the subtraction of

TABLE II. Weight factors for the branches and widths of the rotational lines used in the curve fittings of vibrational lines of the HBr photoelectron spectrum of the $A^2\Sigma^+$ state. The largest weight factor is normalized to 1 for each vibrational state.

Vibrational state v	Rotational width (meV)	Weight factors of rotational branches							
		N	O	P	Q	R	S	T	U
		$\Delta N = -3$	$\Delta N = -2$	$\Delta N = -1$	$\Delta N = 0$	$\Delta N = 1$	$\Delta N = 2$	$\Delta N = 3$	$\Delta N = 4$
0	5.2	0.11	0.05	0.80	0.03	1.00	0.05	0.11	0.04
1	5.2	0.13	0.05	0.80	0.03	1.00	0.04	0.11	0.03
2	5.2	0.14	0.05	0.80	0.04	1.00	0.04	0.11	0.03
3	10.2	0.11	0.06	0.90	0.04	1.00	0.04	0.12	0.03
11	6.2	0.40	0.06	0.99	0.04	1.00	0.03	0.12	0.03
12	6.2	0.76	0.07	1.00	0.05	0.76	0.03	0.14	0.03
13	6.2	0.56	0.06	1.00	0.05	0.63	0.06	0.13	0.03

the background from the $v=4$ line. This may indicate that the lifetime decreases over the energy range of the line. A good fit could be obtained using the data of Table II where particularly the width of the T branch has been much increased.

For lines 11–13, where rotational structure again appears, the curve fittings were less satisfactory as concerned the relative intensities. For line 11 the agreement was still good, but for 12 and 13 the deviations were substantial and seem to be connected to a gradually increasing intensity on the low-binding-energy side. In fact, a good fit of the almost triangular shape of the uppermost lines seems to require a gradual redistribution of intensity to the low-energy rotational branches. The best fitting was obtained for a linewidth of 6.2 meV, i.e., slightly larger than for the lowest states.

Some results of the curve fittings are summarized in Fig. 6.

As can be seen from Table II, the largest intensity is acquired by the P and R branches, i.e., for $\Delta N = \pm 1$, while the Q branch ($\Delta N = 0$) is very weak. This result agrees qualitatively with the results of extensive calculations presented in Ref. [21] for the HF molecule. The main peak of the spectrum therefore essentially reflects the R branch, which is comparatively narrow, while the low-energy tail with the rotational line structure is primarily due to the P branch.

The intensity on the high-binding-energy side of the main peak is associated with the S , T , and U branches. The S branch ($\Delta N = 2$) is weak, but seems to give rise to some intensity at about 8 meV from the zero energy. The strongest structure corresponds to the T branch ($\Delta N = 3$) located about 18 meV from the zero energy. It appears as a broad feature with a rather steep slope on the high-binding-energy side corresponding to the band head. At even higher energy and centered at about 30 meV the U branch ($\Delta N = 4$) gives rise to a very weak structure. On

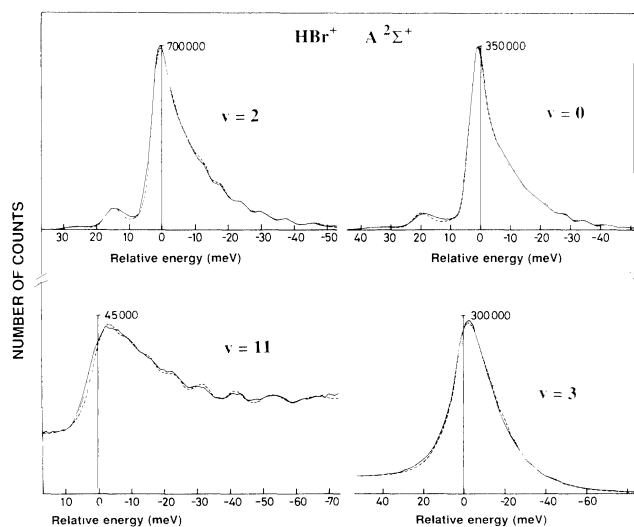


FIG. 6. Selected experimental (full lines) and fitted (dotted lines) spectra showing transitions to the $A^2\Sigma^+$ ($v=0, 2, 3$, and 11) states. The energy scale is given for each line relative to the position of the 0-0 transition.

the low-binding-energy side, the N branch ($\Delta N = -3$) is responsible for a substantial part of the intensity observed as far out as 100 meV from the main peak. However, to account for the total intensity observed on the low-binding-energy side it has been necessary to ascribe a small intensity also to the branches with even ΔN .

V. DISCUSSION

The vibrational lines in the complete spectrum of Fig. 1 apparently form an energetically “normal” progression above the $v=4-8$ region. As indicated above, the calculated vibrational energies agree well with the observed line structure in the low- and high-energy regions of the spectrum. We therefore conclude that the calculated potential curve is well suited for representing the A state except in the region of strong interaction near the curve crossings, that is, in the energy interval between $v=4$ and 9. The interaction with the repulsive states may thus be considered to be localized, at least as regards the influence on the potential curve. As expected, the dissociation continuum is nevertheless significant even above the $v=9$ line, assuming that the increase of the rotational linewidths is due to lifetime broadening.

The rotational linewidths have been used to estimate the lifetime τ of the vibrational states assuming a spectrometer broadening of 5.2 meV as obtained for the $v=0$ and 1 lines. The results are given in Table III. As can be seen, there is a very good agreement with the calculated results of Ref. [1] for the $v=3$ and 4 lines. In the $v=4-9$ energy range, lifetimes of the order of 10^{-14} s were predicted which agrees qualitatively with the large width observed in the spectrum for these lines. Above this region the lifetime increases substantially and is at least in the 10^{-13} s range as obtained from the present spectra. Unfortunately, a comparison between experiment and theory cannot be made for the higher levels due to the lack of theoretical data.

It might seem that the splitting of the rotational branches should become small compared to the linewidth as the lifetime decreases in the region of strong interaction and hence that the lifetime could be obtained by fitting a single, very broad Lorentzian to the observed lines. This is not correct, however. The lines in this energy region contain inherent broad structures that cannot be explained by fitting a single Lorentzian or by the overlap between the lines. Also, fitting of the $v=4$ line with a single Lorentzian gives a background intensity that is far above the observed background between, for example, the $v=2$ and 3 lines. Neither it is reasonable to fit a mixed Gaussian-Lorentzian. Rather, the lines seem to be composed of rotational branches as for the lower vibrational states. Thus the total linewidth of about 130 meV for the $v=4$ line is inappropriate for determination of the lifetime of the state. A correct line shape is not obtained, however, if the line is fitted with the same set of rotational parameters as for the lower, well-resolved peaks, representing essentially the N , P , R , and T branches where P and R are dominating. It appears, for example, that the branches with high values of ΔN on both sides of the Q branch have a much enhanced intensi-

TABLE III. Lifetimes for the vibrational levels of the $A^2\Sigma^+$ state of HBr^+ obtained from the rotational linewidths of Table II and from calculations presented in Ref. [1] by considering predissociation via interaction with the $4\Sigma^-$, $2\Sigma^-$, and 4Π states.

Vibrational level v	Lifetime τ (s) from data of Table II	Lifetime τ (s) from Ref. [1]
0		stable
1		stable
2		1.52×10^{-10}
3	1.3×10^{-13}	1.53×10^{-13}
4	$\approx 1-1.5 \times 10^{-14}$	1.06×10^{-14}
5		1.01×10^{-14}
6		4.40×10^{-14}
7		2.43×10^{-14}
8		2.40×10^{-14}
9		2.91×10^{-14}
10		
11	$\geq 1.9 \times 10^{-13}$	
12	$\geq 1.9 \times 10^{-13}$	
13	$\geq 1.9 \times 10^{-13}$	
14		
15		

ty. However, these observations are difficult to quantify by a simple curve fitting analysis without the support of extensive calculations. The simple analysis shows, however, that a linewidth of the order of 50 meV could be consistent with the observed line shapes. This would correspond to lifetimes of the order of $(1-1.5) \times 10^{-14}$ s in agreement with earlier results [1,8].

In the $v=5-9$ region, the lines exhibit a much broader intensity maximum than other lines of the spectrum. This may suggest that the rotational excitations are not restricted to odd ΔN branches only, but that also the even ΔN branches acquire high intensity. An explanation for a change of this kind could be that the repulsive states mix in new electron configurations which may influence the photoionization cross section for the different rotational branches. Since the line shape is not the same but varies remarkably in this region, the intensity of the branches might depend strongly on energy-dependent variations in the electronic structure.

Finally we may mention that curve fittings were initially attempted without restrictions on the intensity of the different branches. In particular, a high intensity was as-

sumed for the Q branch but these fittings were unsuccessful. Good agreement could be obtained only under the assumption of very low intensity of the Q branch, as well as other branches corresponding to even values of ΔN . This behavior is expected and observed for ungerade states of homonuclear molecules, such as the $B^2\Sigma_u^+$ state of N_2^+ [22]. It may also be understood in the case of HBr if it is assumed that the nature of the $4p\sigma$ orbital of HBr is primarily $\text{Br } 4p$. For photoionization involving $\Sigma^+ \rightarrow \Sigma^+$ transitions it has been shown that $\Delta N + l$ is odd will hold [23], where l signifies the partial wave of the outgoing photoelectron. Thus, since for $4p$ ionization l is expected to be even, ΔN is expected to be odd in agreement with the analysis of the experimental data.

VI. CONCLUSIONS

Well-characterized vibrational levels of the $A^2\Sigma^+$ state of HBr^+ exist up to the dissociation limit. Due to the influence of repulsive interacting states the vibrational lifetime is very short except for the two lowest levels. In the region where the strongest interaction takes place between $v=4$ and 9 the lifetime is of the order of 10^{-14} s. The levels $v=2$ and 3 are strongly predissociated, and a lifetime broadening of the latter state can be observed in the photoelectron spectrum. Above $v=9$ the linewidth decreases and rotational structure can be seen for the $v=11-13$ levels for which a lifetime of about 10^{-13} s has been obtained. The line shape can be explained similarly for all lines with resolved rotational structure in terms of rotational transitions essentially involving branches with odd ΔN . As expected, the $\Delta N = \pm 1$ branches are particularly strong. The main part of the potential curve for the $A^2\Sigma^+$ state can be calculated without consideration of interacting states of different symmetry in a ΛS coupling scheme and only in the region of very strong interaction the influence of the repulsive state curves is of importance.

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