

Excitation of vibrational levels of HF up to $v=4$ by electron impact

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Relative differential cross sections for excitation of vibrational levels of HF up to $v=4$ by slow electron impact have been measured as a function of incident electron energy. Broad oscillatory structures converging to the dissociative attachment threshold, already known in the $v=0\rightarrow 3$ channel, have now also been observed in the $v=0\rightarrow 4$ channel at energies above 1.8 eV. They appear at different energies in the two final channels, revealing their boomerang character. They can be rationalized as a consequence of boomerang motion of the nuclei, initiated either by a broad repulsive σ^* resonance, or resulting from broad overlapping vibrational Feshbach resonances. This observation complements results in other diatomic hydrides and reveals that boomerang structures are present in all members of the series HX ($X=H, F, Cl, Br$), once thought to have no structures of vibrational origin in the cross sections at low energies, because of the extremely short lifetime (or absence) of σ^* resonances. The shape of the $v=0\rightarrow 4$ cross section differs from those of the lower channels also near threshold—it has a weak shoulder at threshold followed by a rounded hump peaking ~ 80 meV above threshold, whereas the cross sections for the $v=1-3$ channels have (within resolution) vertical onsets and narrow peaks at thresholds.

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I. INTRODUCTION

Rohr and Linder [1] discovered unexpected threshold peaks in the vibrational excitation (VE) cross sections of HF and HCl. This discovery initiated a series of experimental and theoretical studies of HF and other hydrogen halides. The experimental work on HF has been continued by Ehrhardt and co-workers with a series of 1989 publications. Knoth *et al.* [2] reported the elastic and the $v=0\rightarrow 1$ cross sections in absolute units at several scattering angles and found the angular distribution near threshold to be nonisotropic. Differential cross sections for rotational and $v=0\rightarrow 1$ rovibrational state-to-state transitions were obtained by Rädle *et al.* [3]. Cross sections for the $v=0\rightarrow 2$ and the $v=0\rightarrow 3$ transitions were reported by Knoth *et al.* [4]. They discovered a deep structure 150 meV below the $v=4$ threshold and assigned it to a nuclear-excited Feshbach resonance (termed vibrational Feshbach resonance in the remainder of this paper [5]). Details of the study of the $v=0\rightarrow 2$ and the $v=0\rightarrow 3$ cross sections were given by Knoth *et al.* [7]. The subject has been reviewed by Ehrhardt [8].

A number of theoretical studies followed the discovery of Rohr and Linder and only an incomplete list is given here. Vibrationally inelastic cross sections have been calculated by Rudge [9] (close coupling) and Rescigno *et al.* [10] (static exchange). An effective-range theory study has been performed by Gauyacq [11], an R -matrix theory study by Morgan and Burke [12]. A static exchange calculation was given by Kutz and Meyer [13]. Vibrational excitation was calculated using a resonant approach by Fabrikant *et al.* [14]. A study of rovibronic excitation has been given by Thümmel *et al.* [15]. A detailed comparison of the experiment and the theory published until 1989 has been given in the publications of Ehrhardt and co-workers cited above.

In the present study we measured the cross sections for vibrational excitation with a magnetically collimated “trochoidal” electron spectrometer, used already in our earlier

study of HCl [16]. This instrument is particularly suitable for the study of threshold features because the collimating action of the axial magnetic field (about 80 G) results in a stable response function even for slow electrons. Its high sensitivity permitted recording the cross sections up to the $v=0\rightarrow 4$ transition.

II. EXPERIMENT

The instrument has been described in Refs. [17–19]. It uses a trochoidal monochromator [20] to prepare a quasimonoenergetic electron beam and two trochoidal analyzers in series to select the energy of the scattered electrons. The electrons collide with a quasistatic gas sample in a collision chamber. The instrument has been improved [21] with respect to our earlier measurement of HCl—the slightly magnetic supporting rods were replaced by titanium rods, significantly reducing the “focussing” artifact. The experiment involves sweeping the incident electron energy and simultaneously the transmittance window of the electron energy analyser (i.e., the residual energy E_r of the detected electrons), keeping the energy difference (i.e., the energy-loss ΔE) constant and equal to the energy of the vibrational level in question. The count rate of the scattered electrons is recorded as a function of the residual electron energy, subsequently corrected for the response function of the energy analyzer, and finally plotted as a function of the incident electron energy. The relative magnitudes of the cross sections are determined from an energy spectrum recorded at a constant residual energy.

The transmissivity of a trochoidal analyzer decreases with increasing energy as a consequence of a decreasing solid angle of acceptance. For residual energies above 0.1 eV the response function has been assumed to be inversely proportional to the residual energy, as in our previous study of HCl [16], except that a better understanding of the helium ionization continuum spectrum as recorded with the magnetically

collimated instrument [22] led us to omit the arbitrary constant factor of 0.15, which was included in the correction equation of the HCl study (Eq. 1 of Ref. [16]). The response function used for correcting spectra below 0.1 eV in present study is derived directly from the helium ionization continuum spectrum, assuming that it is flat when the sum of electrons ejected into 0° and 180° angles is recorded [22]. The present procedure thus differs slightly from that used in the earlier HCl study, the main difference being that it makes the threshold peak about 20% higher (relative to signal at 0.1–2 eV above threshold) than the older procedure. The confidence limits of the correction procedure is taken to be $\pm 20\%$ in the residual energy range 0.1–3 eV and $\pm 35\%$ below 0.1 eV. The spectrometer measures a superposition of forward and backward scattered electrons [18,19]. The angular resolution decreases with decreasing residual electron energy, as discussed in more detail in Ref. [22].

The sample pressure plays a critical role in the present measurements. The very large total scattering cross section of polar molecules at low energies causes noticeable attenuation of slow scattered electrons and consequently a noticeable attenuation or disappearance of the threshold peak already at surprisingly low pressures. Spectra were therefore recorded at successively lower pressures until a pressure was found below which the shape of the excitation functions no longer changed. The pressure in the main chamber of the instrument was then below the sensitivity of the cold cathode gauge, that is less than 10^{-7} mbars, indicating a pressure below 10^{-3} mbars in the target chamber.

The energy-loss scale was calibrated on the HF vibrational peaks, the residual energy scale was calibrated on a sharp resonance feature in the excitation of the 2^3P state of helium which lies at 22.64 eV (residual energy 1.68 eV) in a $0^\circ/180^\circ$ superposition spectrum [19]. It is accurate to within ± 30 meV. The temperature of the target chamber was about 60°C . The excitation functions were measured at the peaks of the vibrational bands, emphasizing $\Delta J=0$ transitions. The resolution (monochromator and analyzer combined) was 60 meV, however, the instrumental band pass was thus comparable to the rotational bandwidth, causing partial integration over rotational transitions.

III. RESULTS

The present VE cross sections are shown in Fig. 1. The shapes of the $v=0\rightarrow 1$ and $v=0\rightarrow 2$ curves agree in essential features with those obtained by Rohr and Linder [1] and Knoth *et al.* [4] (comparing with data not integrated over rotational transitions in the latter paper): a threshold peak, followed by a gradual decrease and a steplike drop at the next vibrational threshold are found in all studies. There are small differences, in particular in the shape of the $v=0\rightarrow 1$ cross section. Rohr and Linder [1] report a very narrow peak followed by a plateau of flat or even slightly rising signal. Knoth *et al.* [4] report a wider threshold peak followed by signal gradually decreasing towards the step at the $v=1$ threshold. The present curve is intermediate in terms of the width of the threshold peak, followed by a plateau of downward sloped signal. The differences are probably due to re-

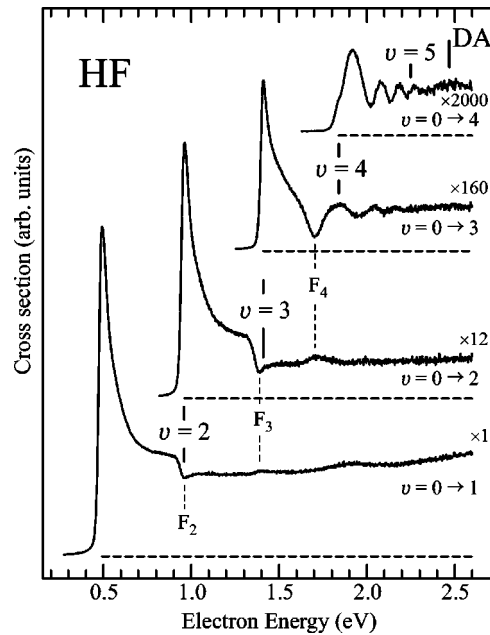


FIG. 1. Cross sections for vibrational excitation in HF, recorded with the magnetically collimated spectrometer. All cross sections are shown on the same (relative) scale, but the curves for the higher vibrational levels are shown vertically expanded as indicated by multiplication factors. The thresholds for dissociative attachment and vibrational excitations are marked by solid vertical lines and labels. Structures indicated by vertical dashed lines and the symbols F_2 – F_4 are discussed in the text.

maining imperfections in the corrections for the response function of the different instruments, to some degree possibly also to different angles of observation.

The shape of the present $v=0\rightarrow 1$ cross section is compared with that of several calculated cross sections in Fig. 2. The theories generally agree well with the experiment in terms of qualitative features, that is a vertical onset, a narrow threshold peak, a gradual fall of the cross section with a downward sloped plateau, and a cusp at the $v=2$ threshold. The calculations of Refs. [12] and [14] also reproduce correctly the weak peak at the $v=3$ threshold. The relative height of the threshold peak can be compared only qualitatively, because it depends on resolution, on the ability of the instrument to detect very slow electrons, and on temperature. With these limitations in mind, the calculations of Refs. [14] and [15] are seen to reproduce the relative height particularly well. The latter study is the only one to take the target temperature explicitly into account, although the present temperature (~ 340 K) is slightly below that assumed in the calculation (400 K).

The shape of the present $v=0\rightarrow 3$ curve (Fig. 1) just above threshold differs somewhat from that of Knoth *et al.* [4]. The present curve has a shape very similar to that of the $v=0\rightarrow 1$ and $v=0\rightarrow 2$ curves, with a quasivertical onset and a peak followed by a downward sloped plateau. Theirs has a more gradual onset and the shape of a nearly symmetrical, relatively broad hump. The two curves agree well above 1.6 eV, however.

The threshold peaks have similar shapes in the lower

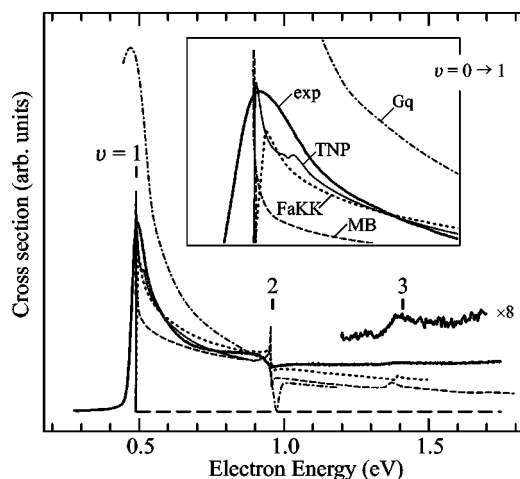


FIG. 2. Comparison of the shape of the experimental $v=0 \rightarrow 1$ cross section with the results of various theories. Shown are: the present data (exp, heavy solid line) and the calculated curves of Gauyacq [11] (Gq, dash-dotted line), Morgan and Burke [12] (MB, dashed line), Fabrikant *et al.* [14] (FaKK, dotted line), and Thümmel *et al.* [15] (TNP, thin solid line). The calculation of Thümmel *et al.* is for target HF at 400 K. The curves are shown on arbitrary vertical scales, normalized at 0.9 eV. (The normalization is only approximate to reduce congestion of lines.) An insert shows a magnified view of the top of the threshold peak.

three curves in Fig. 1 in terms of their vertical onsets (within resolution), their narrow widths (~ 90 meV in all three curves), and the subsequent drop of signal with gradually decreasing slope. A steplike drop of signal is found at the $v=2$ threshold in the $v=0 \rightarrow 1$ curve, about 30 meV below the $v=3$ threshold in the $v=0 \rightarrow 2$ curve, and about 150 meV below the $v=4$ threshold in the $v=0 \rightarrow 3$ curve in agreement with the findings of Ehrhardt and co-workers. A weak peak is further found in the $v=0 \rightarrow 1$ curve about 30 meV below the $v=3$ threshold, that is at the same energy as the above mentioned steplike drop in the $v=0 \rightarrow 2$ curve. A similar but broader weak peak is found in the $v=0 \rightarrow 2$ curve at the same energy as the steplike drop in the $v=0 \rightarrow 3$ curve. An oscillatory structure is found in the $v=0 \rightarrow 3$ curve above 1.7 eV.

The $v=0 \rightarrow 4$ curve has not been reported previously and its shape differs markedly from the three discussed above. It starts with a relatively broad (130 meV), nearly symmetrical hump peaking 80 meV above threshold. A weak shoulder can be discerned on its left side, at the threshold energy. This hump is followed by an oscillatory structure similar to, but deeper than, that found in the $v=0 \rightarrow 3$ curve. In spite of the differences, the shape of $v=0 \rightarrow 4$ curve may represent a continuation of the trends found for the lower curves: the threshold peak has become lower in relative intensity and appears as the shoulder at threshold; the plateau has risen in relative intensity and has become the hump.

The structures above 1.8 eV in the $v=0 \rightarrow 3$ and $v=0 \rightarrow 4$ channels differ from the narrower structures at lower energies described above, as shown in the enlarged view in Fig. 3. They have widths about equal to the widths of the valleys separating them, that is they are not narrow com-

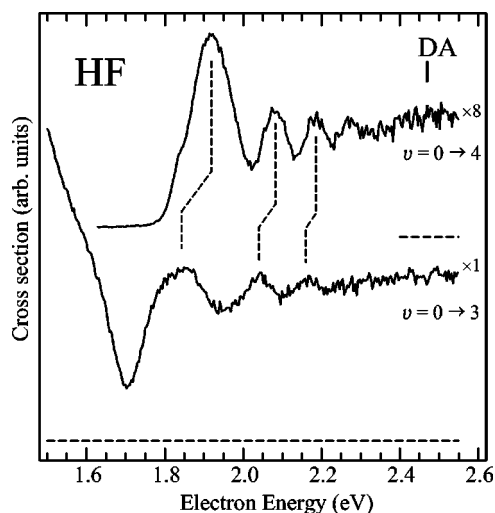


FIG. 3. Detail of the cross sections for excitation of $v=3$ and $v=4$. Broken dashed lines indicate the shift of the structures in the two final channels shown.

pared to their spacing. Most importantly, however, they appear shifted at the two final channels and resemble in this respect the boomerang structures of N_2 .

IV. DISCUSSION

The downward steps and undulatory structures in the cross sections are doubtlessly due to the motion of the nuclei, and are thus of vibrational origin in a broad sense of this term. In the following we shall attempt a classification of the structures based on their experimentally observed properties.

It is well known, and has been described for example by Herzberg [23], that the characteristics of the vibrational structure in cross sections depend sensitively on the autodetachment rate (i.e., lifetime with respect to spontaneous loss of an electron) of the negative ion resonances. A lifetime substantially longer than the classical vibrational period results in vibrational structures which are narrow and which appear *at the same energy in all final channels* in which they are observed (the terms “narrow” and “same energy” are meant within a typical resolution of electron scattering experiments). This case is typically found for vibrational Feshbach resonances, where the vibrational levels of the negative ion lie below the “parent” vibrational levels of the neutral molecule. Autodetachment is slowed down by the fact that it requires a simultaneous decrease of vibrational quantum number. Autodetaching vibrational levels of the $^2\Pi_g$ state [24] of O_2^- may serve as an example; illustrating figures can be found in the work of Linder and Schmidt [25], more recent spectra in Ref. [26].

In contrast, an autodetachment lifetime comparable to classical vibrational period (the boomerang case) results in structures where the peaks have about the same widths as the valleys between them, and which appear *at different energies in different final channels*. A prototype of this case are the well-known boomerang structures of the $^2\Pi_g$ resonance in N_2 [23]. The present results reveal that structures with both characteristics are found in the VE cross sections of HF.

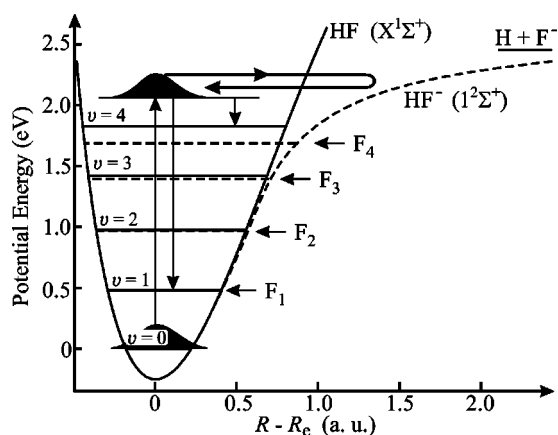


FIG. 4. Schematic potential curves of HF (solid line, with vibrational levels) and the bound part of the HF $^-$ potential curve (dashed line), adopted from Ref. [4]. The boomerang motion of the nuclear wave packet is indicated by a 180° bent arrow.

As pointed out by Knoth *et al.* [4], the structures F_2 , F_3 , and F_4 (Fig. 1) carry the characteristic of the former case and may be assigned as vibrational Feshbach resonances. The structure F_2 is narrow, a width of 15 meV has been found in the higher resolution experiment of Knoth *et al.* [4]. It could also be assigned to a vibrational cusp, however, since it is found at (and not below) the energy of the $v=2$ threshold both in the experiment of Knoth *et al.* [4] and the present experiment (within resolution). The structure F_3 is also narrow and has been found to lie slightly below the $v=2$ threshold both in the experiment of Knoth *et al.* [4] and the present experiment. Furthermore, a structure is observed at the same energy in two channels, $v=0 \rightarrow 1$ and $v=0 \rightarrow 2$ (Fig. 1). It can thus be assigned as a vibrational Feshbach resonance with the $v=3$ level of neutral HF as the parent state. The structure F_4 is broader than F_2 and F_3 but still narrower than the spacing between F_3 and F_4 , and has been found at the same energy in two channels, $v=0 \rightarrow 2$, and $v=0 \rightarrow 3$. It can thus be assigned as a broadened vibrational Feshbach resonance with the $v=4$ level of neutral HF as the parent state.

The situation is illustrated by the qualitative potential curves in Fig. 4. The bound negative ion potential curve approaches the neutral potential curve from the right, then proceeds nearly parallel with it, and energetically just below it for a certain range of internuclear distances, and finally disappears when the electron is no longer bound. We do not have the means to determine at which internuclear distance does the HF $^-$ potential curve disappear. The dipole moment function calculated by Werner and Rosmus [27] indicated dipole moment larger than critical and thus ability of HF to bind an electron down to $R \approx 1.5$ a.u. A potential energy curve for HF $^-$ which lies below that of neutral HF at all geometries down to $R=1.65$ a.u. was also calculated by Morgan and Burke [12]. On the other hand, the calculation of Gutowski and Skurski [28] and the failure of Hendricks *et al.* to observe stable HF $^-$ experimentally [29] would indicate that the bound part of the HF $^-$ potential curve does not extend below R_e , the bottom of the HF curve. A bound HF $^-$

potential curve extending below R_e and the failure to observe bound HF $^-$ experimentally are not necessarily contradictory, however, since Garrett [30] has shown that molecular rotation smears out the dipole potential and a rotating HF molecule (even with $J=0$) may not be able to bind an electron even when the potential curve, defined for fixed nuclei, is bound. (On the other hand a *very* weakly bound electron could also be detached by the unavoidable electric fields in a real experiment, preventing the observation of a very weakly bound HF $^-$ in a mass spectrometer.)

The inability of HF to bind an electron at short R_e may seem to cause a problem with the assignment of the structures F_2 – F_4 to vibrational Feshbach resonances. The question arises whether structures bearing the experimental characteristics of vibrational Feshbach resonances in the sense described above can be found even without a bound negative ion potential curve extending over a large range of internuclear distances on which the nuclear wave packet can move back and forth many times to develop narrow vibrational features. Theory does account for narrow vibrational Feshbach resonances even on such negative ion potential curves, “open” at short R , for example, in HCl [31] and CH $_3$ I [6]. The qualitative explanation is that the electron departs only slowly while the nuclear wave packet moves at short R (where the electron is not bound), and is recaptured with large probability when the nuclei swing back to large R where the electron is bound.

The present observation of boomerang structures above 1.8 eV in the $v=0 \rightarrow 3$ and $v=0 \rightarrow 4$ channels of HF shown in Fig. 3 indicates that autodetachment lifetime is short compared to the classical vibrational period above 1.8 eV, preventing the multiple back and forth motion of the nuclear wave packet required for development of narrow vibrational features. A qualitative picture involves a boomerang motion of the nuclei, where the outgoing nuclear wave packet is reflected on the bound potential curve of HF $^-$ at large R and nearly annihilated by fast autodetachment at short R (preventing further reflections) as indicated by the 180° bent arrow in Fig. 4.

The repulsive force required to set the nuclear wave packet into outward motion could be provided by a repulsive σ^* resonance, analogous to the π^* resonance in the prototype boomerang case N $_2^-$. (A quantitative calculation within the nonlocal resonance model would presumably invoke a backfolding potential curve connecting the crossing point and the repulsive part of the σ^* resonance, similar to the one shown in Fig. 3.7 of the review by Domcke [32].)

An alternate explanation would view the boomerang structures as a remainder of vibrational Feshbach resonances which become broader with increasing energy until they start to overlap at energies above 1.8 eV. The increasing width is a consequence of increasing probability of electron loss at the inner turning point, which moves to shorter R with increasing energy. The nuclear wave packet is nearly annihilated at the inner turning point above about 1.8 eV and a boomerang motion of the nuclei results. It may not be proper to use the term of vibrational Feshbach resonances at energies above 1.8 eV, however, since the boomerang structures can no longer be associated with definite vibrational quan-

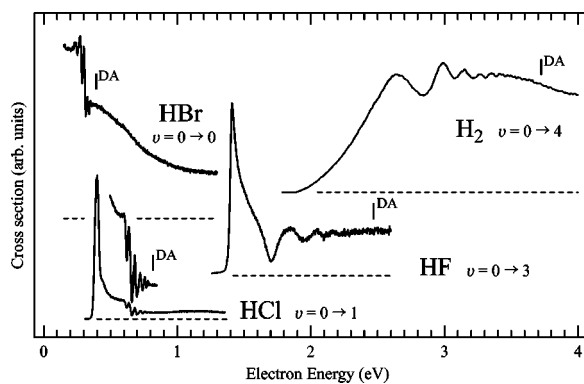


FIG. 5. Illustration of the boomerang structures in the four diatomic hydrides HBr [35], HCl [34], HF (present work), and H_2 [36]. Elastic cross section is shown for HBr, where the structure is located below the lowest vibrational excitation threshold. The cross sections for HF and H_2 are shown for the lowest transitions where clear boomerang structure is observed.

tum numbers and the parent-daughter relation inherent to the definition of a Feshbach resonance is lost.

Rescigno *et al.* [33] and Morgan and Burke [12] did not find evidence for a resonance below 3 eV in their *ab initio* calculations, and their result would thus favor the latter explanation of the boomerang structures. A slow rise of the eigenphase sum due to a very broad resonance could be hidden under the background eigenphase sum, which drops rapidly with energy in the *ab initio* calculations, however.

Finally, it appears to us that the two explanations have many aspects in common and need not be mutually exclusive. The “extra” electron is located near the H end of the HF molecule in both cases, because of the larger coefficient of the σ^* orbital at the H atom in the one case, and because of the binding by the positive end of the dipole in the other. In both cases is the electron temporarily bound in the vicinity of the HF molecule, causing the vibrational excitation. The temporary binding is caused by a centrifugal barrier due to the (small) contribution of p wave in the case of a broad σ^* resonance, and by the recapture of the departing electron by the vibrating nuclei in the case of overlapping vibrational Feshbach resonances. The reality may well include both aspects.

The present measurement of HF complements the data available for a series of related compounds. Their comparison, shown in Fig. 5, reveals undulatory structures with striking similarities and continuous trends in the three halogen hydrides up to HBr and even in H_2 itself. Boomerang structures are now seen in four compounds, once thought to have resonances too short lived to cause structure of vibrational origin. The similarities of the spectra strongly suggest that basically the same physical mechanism is operating in all four molecules as far as boomerang structures are concerned. We thus assume that the fundamental cause of the structures must be a property of the target which is common to all four molecules.

The same type of structure is observed in spite of the fact that the dipole moment and polarizability vary widely: the dipole moment of HF is supercritical, those of HBr and HCl

below critical, that of H_2 is zero; the polarizabilities of HBr and H_2 differ dramatically. The only aspect common to all molecules is a bound potential curve rising with R on which an outgoing nuclear wave packet can be reflected, and fast autodetachment at short R , preventing multiple reflections. (The situation in HCl and HBr is slightly complicated by narrow outer well resonances superimposed on the broader boomerang structure [34].)

Note that the boomerang interpretation can rationalize qualitatively an interesting aspect of the observations: Clear boomerang structures can be observed already in the $v=0 \rightarrow 1$ cross section in HCl, but are not visible until the $v=0 \rightarrow 3$ cross section in HF, and $v=0 \rightarrow 4$ cross section in H_2 . Franck-Condon (FC) principle has the consequence that higher final vibrational levels are excited by transitions at larger internuclear distances, that is closer to the stabilization point, whereas transitions to lower final levels (e.g., $v=1$ in HF or H_2) occur at shorter internuclear distances, farther away from the stabilization point (vertical arrows in Fig. 4). The amplitudes of the outgoing and the reflected waves are very different at a point far on the left of the stabilization point (thus precluding interference), since the wave packet has to travel longer on parts of the potential curve with fast autodetachment. The amplitudes of the outgoing and the reflected waves are similar at an R close to the stabilization point, permitting interference and thus deep structures in the cross sections for excitation of high vibrational levels. The stabilization point lies far from the FC region in molecules with DA threshold high in energy (such as H_2 or, to a lesser degree, HF), it is close to the FC region in HBr or HCl.

V. CONCLUSIONS

Structures with two different qualitative characteristics are found in the vibrational excitation cross sections in HF. Relatively narrow structures (F_2-F_4 in Figs. 1 and 4) in the form of downward steps or weak peaks are found below 1.8 eV with the final channels up to $v=3$. We agree with the conclusion of Knoth *et al.* [4] that their properties justify an assignment to vibrational Feshbach resonances.

Structures above 1.8 eV in the cross sections for exciting $v=3$ and $v=4$ are broader and appear at different energies in the two channels. They thus resemble the structures caused by the ${}^2\Pi_g$ resonance in N_2 and we consequently assign them to boomerang motion of the nuclei, reflected on the bound part of the HF^- potential curve (Fig. 4) and subsequently annihilated by fast autodetachment at short R . The nuclei could be first repelled by a broad σ^* resonance (in analogy to the π^* resonance in the prototype boomerang case N_2^-), or the boomerang structures could emerge from broad overlapping vibrational Feshbach resonances, without the necessity to invoke a σ^* resonance. Boomerang structures are thus observed in a molecule with potential curve of the negative ion substantially different from that of the prototype N_2^- case and theoretical work on the excitation of the higher vibrational levels of HF will be required to provide a clear physical picture of their origin.

A systematic view of phenomena encountered in electron scattering in diatomic hydrides is obtained when the present

data are combined with earlier results. In particular boomerang structures converging to the dissociative attachment threshold are seen to be no exception, they are found in all four compounds shown in Fig. 5. An interesting trend appears—the boomerang structures are prominent already in the elastic and the $v = 1$ channels in HBr and HCl, but only in progressively higher vibrational channels in HF and H₂. This trend can be rationalized qualitatively as a consequence of an increasingly longer path and consequently longer time which the nuclei have to travel to reach the stabilization point, and thus go hand in hand with the decreasing cross section for dissociative electron attachment. (A related parallel has been found in the HBr/DBr pair between the magnitude of dissociative attachment cross section and the depth

of boomerang structure in the elastic cross section [35].)

Finally we point out that since the widths and exact energies of the structures are of central importance, deeper insight could be gained by experiments utilizing photoionization electron beam sources having sub-meV resolution [6].

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- [1] K. Rohr and F. Linder, *J. Phys. B* **9**, 2521 (1976).
 [2] G. Knoth, M. Rädle, M. Gote, H. Ehrhardt, and K. Jung, *J. Phys. B* **22**, 299 (1989).
 [3] M. Rädle, G. Knoth, K. Jung, and H. Ehrhardt, *J. Phys. B* **22**, 1455 (1989).
 [4] G. Knoth, M. Gote, M. Rädle, K. Jung, and H. Ehrhardt, *Phys. Rev. Lett.* **62**, 1735 (1989).
 [5] We follow the recommendation of Hotop *et al.* [6] and prefer the term vibrational Feshbach resonances to the older term nuclear excited Feshbach resonances to avoid implying internal excitation of the nuclei.
 [6] A. Schramm, I.I. Fabrikant, J.M. Weber, E. Leber, M-W. Ruf, and H. Hotop, *J. Phys. B* **32**, 2153 (1999).
 [7] G. Knoth, M. Gote, M. Rädle, F. Leber, K. Jung, and H. Ehrhardt, *J. Phys. B* **22**, 2797 (1989).
 [8] H. Ehrhardt, *Aspects of Electron-Molecule Scattering and Photoionization*, edited by A. Herzenberg AIP Conf. Proc. **204** (AIP, New York, 1989), p. 145.
 [9] M.R.H. Rudge, *J. Phys. B* **13**, 1269 (1980).
 [10] T.N. Rescigno, A.E. Orel, A.U. Hazi, and B.V. McKoy, *Phys. Rev. A* **26**, 690 (1982).
 [11] J.P. Gauyacq, *J. Phys. B* **16**, 4049 (1983).
 [12] L.A. Morgan and P.G. Burke, *J. Phys. B* **21**, 2091 (1988).
 [13] H. Kutz and H.-D. Meyer, *J. Phys. B* **23**, 829 (1990).
 [14] I.I. Fabrikant, S.A. Kalin, and A.K. Kazansky, *J. Phys. B* **25**, 2885 (1992).
 [15] H.T. Thümmel, R.K. Nesbet, and S.D. Peyerimhoff, *J. Phys. B* **26**, 1233 (1993).
 [16] A. Schafer and M. Allan, *J. Phys. B* **24**, 3069 (1991).
 [17] M. Allan, *Helv. Chim. Acta* **65**, 2008 (1982).
 [18] M. Allan, *J. Electron Spectrosc. Relat. Phenom.* **48**, 219 (1989).
 [19] K.R. Asmis and M. Allan, *J. Phys. B* **30**, 1961 (1997).
 [20] A. Stamatović and G.J. Schulz, *Rev. Sci. Instrum.* **41**, 423 (1970).
 [21] K. R. Asmis, Ph.D. thesis, Fribourg, 1996.
 [22] K.R. Asmis and M. Allan, *J. Phys. B* **30**, L167 (1997).
 [23] A. Herzenberg, *Electron-Molecule Scattering and Photoionization*, edited by P. G. Burke and J. B. West (New York, Plenum, 1984), p. 187.
 [24] The ${}^2\Pi_g$ state of O_2^- is a shape resonance in terms of its electronic structure. Its vibrational levels with $v' \geq 4$ are vibrational Feshbach resonances, however, because they lie energetically below their parent vibrational states of the ${}^3\Sigma_g^-$ electronic ground state of O_2 .
 [25] F. Linder and H. Schmidt, *Z. Naturforsch. A* **26A**, 1617 (1971).
 [26] M. Allan, *J. Phys. B* **28**, 5163 (1995).
 [27] H.-J. Werner and P. Rosmus, *J. Chem. Phys.* **73**, 2319 (1980).
 [28] M. Gutowski and P. Skurski, *J. Chem. Phys.* **107**, 2969 (1997).
 [29] J.H. Hendricks, H.L. de Clercq, S.A. Lyapustina, and K.H. Bowen, Jr., *J. Chem. Phys.* **107**, 2962 (1997).
 [30] W.R. Garrett, *J. Chem. Phys.* **73**, 5721 (1980).
 [31] J.P. Gauyacq and A. Herzenberg, *Phys. Rev. A* **25**, 2959 (1982).
 [32] W. Domcke, *Phys. Rep.* **208**, 97 (1991).
 [33] T.N. Rescigno, A.E. Orel, A.U. Hazi, and B.V. McKoy, *Phys. Rev. A* **26**, 690 (1982).
 [34] M. Čížek, J. Horáček, M. Allan, and W. Domcke, *J. Phys. B* **33**, L209 (2000).
 [35] M. Čížek, J. Horáček, A.-C. Sergenton, D. Popović, M. Allan, and W. Domcke (unpublished).
 [36] M. Allan, *J. Phys. B* **18**, L451 (1985).