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Vibrationally resolved photoelectron angular distributions for H_2 in the range $17\ \text{eV} \leq h\nu \leq 39\ \text{eV}$

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Vibrationally resolved photoelectron angular distributions have been measured for photoionization of H_2 over the range $17\ \text{eV} \leq h\nu \leq 39$ eV using independent instrumentation at two synchrotron radiation facilities. The present data greatly extend and add vibrational resolution to earlier variable-wavelength measurements. The average magnitude of the asymmetry parameter continues to lie lower than the best independent-electron calculations. Broad structure is observed for the first time, possibly indicating the effects of channel interaction with dissociative, doubly excited states of H_2. Neither the average magnitude nor the gross wavelength-dependent structure vary strongly with the final vibrational channel.

I. INTRODUCTION

Most attempts to extend our basic understanding of molecular photoionization and related processes have focused on molecular hydrogen, primarily because it is the simplest molecule which is both theoretically and experimentally tractable. In many instances, this system provides our best opportunity to gain insight into fundamental molecular behavior, such as the interactions among electronic and nuclear modes and motion of excited electrons in an anisotropic field. To be sure, great strides have been made, particularly in the analysis[1–10] of complex structure in the photoabsorption[2] and photoionization[11] cross sections by the multichannel quantum-defect theory (MQDT). Moreover, predictions[6,8–10] have been made for the effects of autoionization on rotational and vibrational branching ratios and photoelectron angular distributions, and the competition between photoionization and photodissociation has been considered[12] in a unified manner.

These very satisfying studies of H_2 could easily lead one to believe that the vacuum-ultraviolet (vuv) photoionization dynamics of H_2 are well in hand. However, shortcomings in our understanding are easily found in the study of a complementary quantity—photoelectron angular distributions in the open continuum, from the ionization potential (IP) to tens of eV above it. The dozens of studies over 20 years have revealed a persistent disagreement between experiment[13–25] and theory.[9,10,26–49] Nearly all theoretical treatments have employed independent-electron models using various levels of approximation for the initial state, the final state, and the treatment of the internuclear distance R which is either fixed or varied adiabatically. Broadly speaking, these calculations yield a large value of $\beta \sim 1.9$ for the photoelectron asymmetry parameter, very near the maximum value $\beta = 2$. Only recently have calculations[41,42,46] been extended to include channel interaction with doubly excited, dissociative states converging to repulsive states of $H_2{}^+$. These calculations show that such interactions can cause marked deviations from the large asymmetries indicated earlier; however, the small set of fixed-R calculations exhibit sharp R dependence, and are still inadequate to indicate the net result of averaging over nuclear motion. A realistic calculation, including all relevant electronic channels and proper treatment of nuclear motion, is still very difficult and has yet to be carried out over the energy range of interest here.

The many experimental results also give a mixed and incomplete picture, and one that differs significantly from theoretical predictions to date. In particular, the results using synchrotron radiation[19,21,25] give a substantially lower value of β over the first 10–15 eV above the IP. The recent study by Southworth *et al.*[21] yielded an average value for H_2 of $\beta \sim 1.7$, whereas the earlier values by Marr *et al.*[19] were even lower. The β measurements obtained at selected wavelengths using resonance lines gave mixed results. Some reproduce the lower values observed with synchrotron radiation. Others yield higher values, much closer to theory.

We have therefore remeasured the β for H_2, extending the experimental evidence on this important and controversial topic in two respects. First, we have greatly extended the wavelength coverage by combining data taken at two synchrotron radiation facilities, using a normal-incidence monochromator for the range 16.8 eV$\leq h\nu \leq$26 eV at the National Bureau of Standards and a toroidal grating monochromator for the range 26 eV$\leq h\nu \leq$39 eV at Daresbury Laboratory. Second, the present data are resolved into alternative final vibrational channels, as this is often much more sensitive to underlying dynamics (particularly resonances) than vibrationally unresolved data. We anticipate our results by noting that the present data reinforce the differences between experiment and independent-electron theories and suggest, both through the observed absolute values and incipient structure, that a more sophisticated picture, almost certainly including R-dependent interaction with doubly excited channels, must be employed.

II. EXPERIMENTAL PROCEDURE

The present data are comprised of two sets measured independently at two synchrotron radiation facilities. The data in the range 16.8 eV$\leq h\nu \leq$26 eV were measured on the 2-m, normal-incidence monochromator[50] at the Synchrotron Ultraviolet Radiation Facility (SURF) at the National Bureau of Standards (NBS). The data in the range 26 eV$\leq h\nu \leq$39 eV were measured on the toroidal grating monochromator at the Daresbury Laboratory Synchrotron Radiation Source (SRS).

The electron spectrometer system[51] at NBS consists of two hemispherical analyzers (10.2 cm mean radius), operated simultaneously at observation angles of 0° and 90° relative to the major polarization axis of the photon beam. Each analyzer employs a position-sensitive area detector at the exit plane of the hemispheres in order to increase sensitivity by simultaneously detecting a range of electron energies. Each energy spectrum is scanned so that all portions of the area detector are exposed to each energy, thus eliminating any nonuniformity of response. The spectrometers were operated with 5 eV pass energy, resulting in a resolution of ~0.060 eV. When combined with the 0.65-Å bandpass of the monochromator, this resulted in sufficient net electron energy resolution to easily resolve the vibrational components of the photoelectron spectrum of H_2. For instance, at 21.21 eV the monochromator bandpass (0.024 eV) and the electron spectrometer resolution (0.060 eV) combined to yield an observed 0.065-eV photoelectron peak width, to be compared with ω_e=0.288 eV for $H_2{}^+$. The electron spectrometer system used at Daresbury consisted of a single electron analyzer which was rotated between two angles (parallel and normal to the major polarization axis of the light) in order to measure photoelectron angular distributions. This spectrometer also employs an area detector to enhance sensitivity and was operated at approximately 0.080 eV resolution in order to resolve vibrational structure in the photoelectron spectrum of H_2. For example, at 26 eV the monochromator bandpass was 0.050 eV, resulting in a net photoelectron peak width of ~0.090 eV. In both instruments, the ionization region and entire photoelectron flight path were shielded from magnetic and stray electric fields. The experiments were conducted at sample pressures demonstrated to cause no effect on the ratio of intensities at the two observation angles. The background pressure in the vacuum chamber was $\sim 1.9\times10^{-5}$ and $\sim 6.5\times10^{-6}$ Torr for the NBS and Daresbury measurements, respectively. The pressure in the ionization region is estimated to be ~10–100 times higher.

The differential cross section for photoionization of a randomly oriented target in the dipole approximation is

$$\frac{d\sigma}{d\Omega}=\left[\frac{\sigma_{\rm tot}}{4\pi}\right]\{1+(\beta/4)[1+3p\cos(2\theta)]\}\ , \tag{1}$$

where $\sigma_{\rm tot}$ is the total photoionization cross section, β is the asymmetry parameter, $p=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$ is the polarization of the light, and θ is the photoelectron ejection angle relative to the major polarization axis of the light. In the present measurements, photoelectron intensities are measured at two angles, yielding

$$\frac{I(\theta_1)}{I(\theta_2)}=c\frac{\{1+(\beta/4)[1+3p\cos(2\theta_1)]\}}{\{1+(\beta/4)[1+3p\cos(2\theta_2)]\}}\ . \tag{2}$$

Determination of β therefore requires measurement of the ratio $I(\theta_1)/I(\theta_2)$ and independent knowledge of the polarization p and the angular correction factor c which represents the relative efficiencies of the electron spectrometer(s) at the two observation angles. The latter factor is typically very close to unity, within a few percent, and results from lack of cylindrical symmetry of the ionization region, due to the intersection of a diffuse gas source and a flat horizontal light beam, as well as other minor differences at the two angles.

The calibration procedures varied somewhat for the two sets of measurements. At NBS, the polarization was measured using a triple-reflection polarization analyzer and was found to be independent of wavelength, within measurement uncertainty, over the range 16.8 eV $\leq h\nu \leq$26 eV. Since the accuracy of such a polarization analyzer depends critically on the reflectivity of the gold plated mirrors, we calibrated the absolute value of the polarization with He gas, in order to eliminate errors due to surface conditions which can change over time. The He-based polarization was effected in two steps. First, photoelectron spectra for Ar were recorded slightly less than 1 eV above the ionization limit where β=0. When β=0, c can be determined directly from Eq. (2), independently of the polarization. Second, photoelectron spectra for He were measured for photoelectrons with the same kinetic energy. Since c for this kinetic energy was determined in the first step, the relative photoelectron intensities for He, together with its known photoelectron asymmetry, β=2, determines the absolute value of the polarization. This procedure produced a value of p=0.67, with an uncertainty slightly under ±0.03. The present results are thus anchored to the known value of β=2 for He through the polarization determination. Unfortunately, He could not be used to calibrate the angular correction factor c throughout the kinetic energy range of interest, due to the wavelength limitations of a normal-incidence monochromator.

TABLE I. $Ar^+ \, {}^2P_{1/2,3/2}$ asymmetry parameters.

$h\nu$	β
16	-0.14 ± 0.05
17	0.12 ± 0.05
18	0.34 ± 0.05
19	0.56 ± 0.05
20	0.72 ± 0.05
21	0.84 ± 0.05
22	0.98 ± 0.05
23	1.08 ± 0.05
24	1.18 ± 0.05
25	1.24 ± 0.05
26	1.32 ± 0.07

Hence, the angular calibration over the range of interest was achieved by measuring the relative intensities of photoelectrons at $\theta=0°$ and 90° for the process $Ar + h\nu \rightarrow Ar^+ \, {}^2P_{1/2,3/2} + e$. The angular calibration factor was then determined from Eq. (2) by use of well-characterized values for the asymmetry parameter for this process. The β values for Ar used in this work are taken from Ref. 52 and are summarized in Table I. This calibration procedure was also found to produce β values for Kr and Xe in good agreement with those reported in Ref. 52. Once the values of p and c are so determined, intensity measurements at two angles directly yield an absolute β value according to Eq. (2). Argon calibration runs were performed both before and after the series of H_2 runs reported here. The two calibrations were identical.

For the Daresbury measurements, it was practical to use He ($\beta=2$) as a calibration standard, obviating the need for a secondary standard. Moreover, the detection efficiency was found to be remarkably independent of angle so that $c\sim1$. This led to a calibration procedure in which measurements of photoelectron intensities for He at two angles led to a determination of p, which was found to vary from ~0.76 to ~0.64 over the range 26 eV $\leq h\nu \leq$ 39 eV. Helium calibrations were performed either immediately before or immediately after each data point and within the same beam fill.

In order to determine vibrationally resolved $\beta(v)$, the photoelectron spectra recorded at each wavelength had to be resolved into vibrational components. Although the vibrational bands were rather well resolved, each spectrum was decomposed two ways to assure accurate vibrational intensities at the two observation angles. Specifically, the data were analyzed both by nonlinear curve fitting and by simple histogram summing of the counts in each peak, after subtracting the small sloping background which was nevertheless important to treat carefully owing to the large value of β in this case. The nonlinear fits utilized Gaussian and skewed Gaussian peak shapes for the NBS and Daresbury data sets, respectively. For both data sets, the parallel analyses agreed very well and the curve-fitting results are reported here, as they automatically kept track of error accumulation and produced realistic uncertainties.

Principal sources of errors in the present results are statistical uncertainties, polarization uncertainties, errors in the secondary standard, and errors in data fitting or summing procedures. In various ways, these are exacerbated by hydrogen's small cross section, high values of β, and unresolved rotational structure and anharmonicity which make background determination more problematic than it ordinarily is. These errors have been estimated and their effects propagated through the calculation to yield realistic error bars for the data.

III. RESULTS

The present measurements of the asymmetry parameter for molecular hydrogen are presented in Fig. 1 (vibrationally averaged) and Fig. 2 (vibrationally resolved). In both figures, the data taken at NBS (16.8 eV $\leq h\nu \leq$ 26 eV) and those taken at Daresbury (26 eV $\leq h\nu \leq$ 39 eV) are represented by solid circles and solid squares, respectively. Note that there exists very good agreement between the NBS and Daresbury measurements for both β_{av} and $\beta(v)$ at $h\nu=26$ eV, where the two data sets overlap. In fact, at this energy the results of four independent synchrotron measurements (present NBS and Daresbury measurements, plus Refs. 21 and 25) for β_{av} are in excellent agreement, as seen in Fig. 1.

Vibrationally averaged results of three earlier studies based on synchrotron radiation are included in Fig. 1. The data from the early study by Marr *et al.*[19] are found to fall significantly below the growing body of data from other measurements. The values reported by Southworth *et al.*[21] lie somewhat below, usually within 0.15, whereas the β_{av} values reported by Yagishita *et al.*[25] are in good agreement with the present data, except at the highest energy point ($h\nu=30$ eV) which indicates a strong downward step, in contrast to the present data which exhibit a maximum at that energy.

An extensive literature,[13-18,20,22-24] starting 20 years ago, exists on photoelectron asymmetries in H_2 measured with resonance radiation. Most of these data are included in Figs. 1 and 2 for comparison with the present data. The congestion at 21.2 eV prohibits clear distinction of individual points; however, detailed tabular comparison has been made in several recent articles.[20,23,33,47,49] [In cases where β_{av} was not reported, but several $\beta(v)$ were, we have synthesized β_{av} for Fig. 1 by averaging over $\beta(v)$ weighted by the Franck-Condon factors reported by O'Neil and Reinhardt.[53]] The He II (40.8 eV) resonance line represents an important independent reference point at the high-energy limit of the present data. There the β_{av} and $\beta(v)$ data mesh smoothly with the He II measurements by Poliakoff *et al.*[23] and by Katsumata *et al.*,[17] although the latter data have very large uncertainties. Similarly, very good agreement with the Ne II (26.9 eV) results of Poliakoff *et al.*[23] is observed. The situation at the most frequently used He I (21.2 eV) resonance line is more complex. There, the six resonance line studies span a range of ~0.2 β units, a range too large to be useful in resolving the existing controversy. Referring to Fig. 1, however, we note that most of the β_{av} data at 21.2 eV overlap, within stated er-

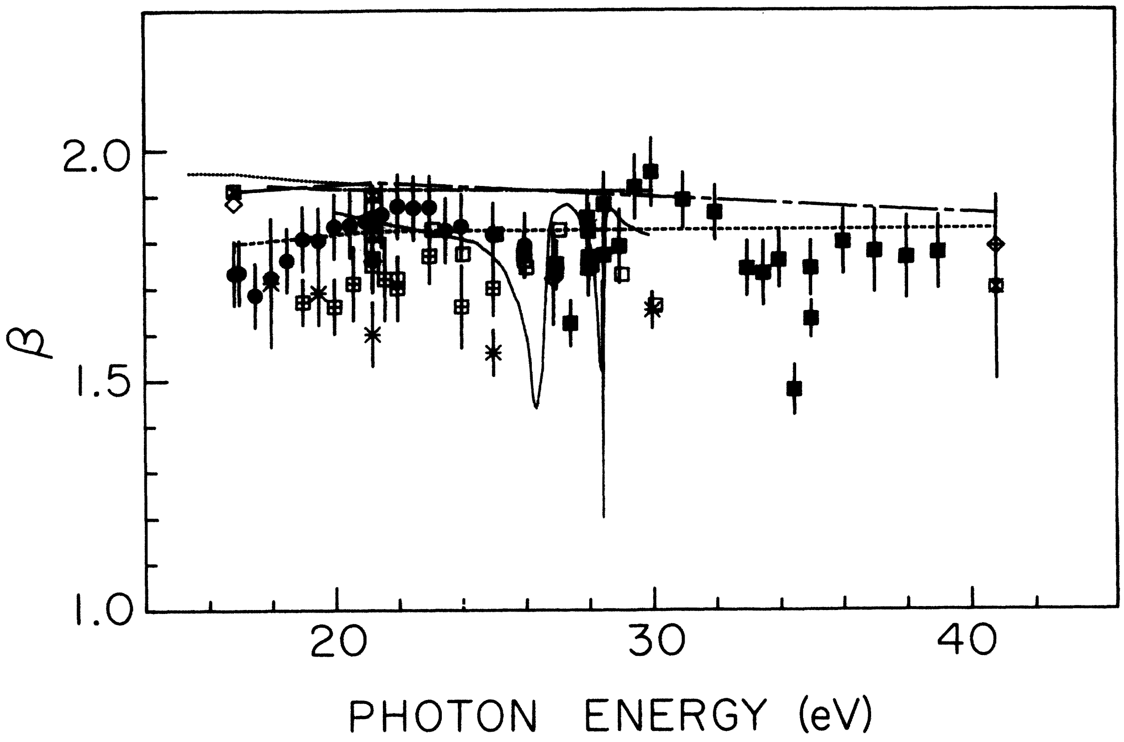

FIG. 1. Vibrationally averaged photoelectron asymmetry parameter for H_2. Experiment: ●, present data, taken at NBS; ■, present data, taken at Daresbury Laboratory; ✱, Marr *et al*, Ref. 19; ⊞, Southworth *et al.*, Ref. 21; ◈, Poliakoff *et al.*, Ref. 23; ⊗, Katsumata *et al.*, Ref 17; ⧗, Kreile and Schweig, Ref. 20; ⊠, Ruf *et al.*, Ref. 24, as derived by Hara *et al.*, Refs. 43, 44, and 47; □, Yagishita *et al.*, Ref. 25; ⊕, Carlson and Jonas, Ref. 15. Theory: — — —, Itikawa, Ref. 33; –·–, Collins and Schneider, Ref. 40; ———, Hara *et al.*, Refs. 43, 44, and 47; · · ·, Raseev, Ref. 41; ——, Raseev, Refs. 41 and 42; ◇, Raoult *et al.*, Ref. 10.

rors, the $\beta_{av}=1.85\pm0.07$ value reported here. This includes the $\beta_{av}=1.902\pm0.01$ value, reported by Hara *et al.*,[43,47] which is based on an analysis of the angle dependence of rotational branching ratios measured by Ruf *et al.*[24] This higher value agrees well with the best independent-electron calculations. At the Ne I resonance line, a similar analysis of rotational branching ratios measured by Ruf *et al.*[24] ($v=0-3$) and by Pollard *et al.*[22] ($v=0$) results in values significantly above the present values, while the $\beta(v=0)=1.67\pm0.05$ value by Poliakoff *et al.*[23] lies below the present datum.

The corresponding theory also has an interesting history, dating from 1968. We have summarized the soundest theoretical results in Figs. 1 and 2 in the following manner. Figure 2 includes $\beta(v)$ results by Itikawa,[33] Hara *et al.*,[43,44,47] Tennyson *et al.*,[46] and Raoult *et al.*[10] The resonance line results calculated by Itikawa[33] and by Hara *et al.*[43,44,47] have been connected by lines to create a better visual impression. Recent results by Itikawa *et al.*[39] are practically indistinguishable from those of Hara *et al.*[43,44,47] In Fig. 1, representative results by Itikawa,[33] Collins and Schneider,[40] Hara *et al.*,[43,44,47] and Raseev[41,42] are represented by lines, and the datum by Raoult *et al.*[10] is given individually. Calculations by Chandra,[49] Tennyson *et al.*,[46] Richards and Larkins,[45] and Itikawa *et al.*[39] agree well with the three higher theoretical curves and thus were omitted to avoid excessive congestion. The solid line in Fig. 1 is a fixed-*R* calculation by Raseev[41,42] indicating the effect of channel interaction with three doubly excited states of H_2, converging to dissociative ionic states. An analogous calculation by Tennyson *et al.*[46] shows similar resonant structure at different values of internuclear separation. These calculations are discussed further below.

IV. DISCUSSION

Two main observations can be made regarding the results in Figs. 1 and 2, one concerning the average magnitude of β over this energy range and the other concerning the structure in the wavelength dependence of β. Perhaps the most concrete conclusion can be drawn by looking at the gross average magnitude of β_{av} over the entire spectral range in Fig. 1. There we see that the present measurements lie below the results of the best single-channel-model calculations, namely, those represented by Collins and Schneider[40] Hara *et al.*,[43,44,47] and Raseev.[41] The better agreement between the experimental data and the earlier calculation by Itikawa[33] must be discounted due to the neglect of exchange and polarization in those calculations. To be precise, the spectral average of all of the present data in

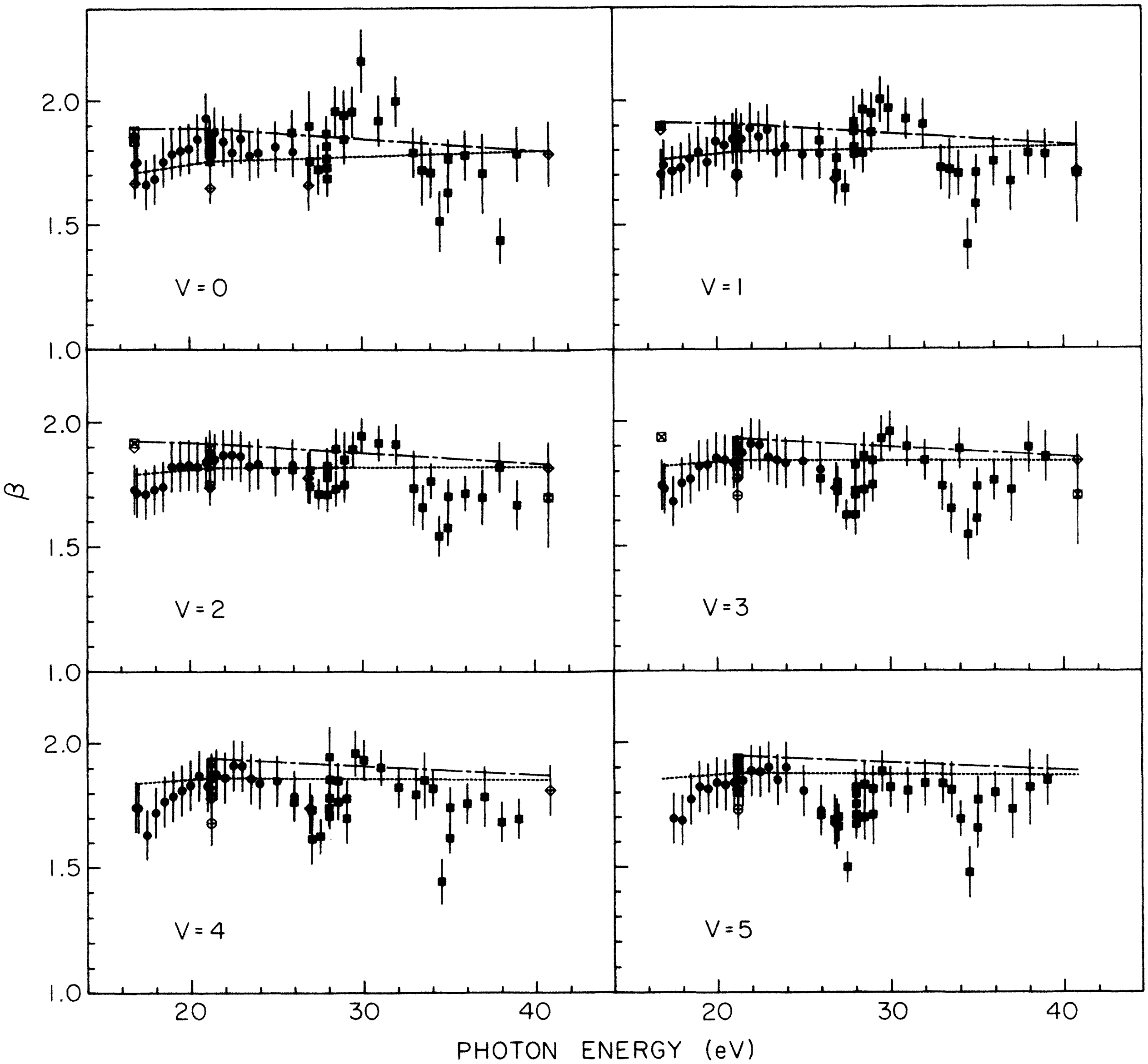

FIG. 2. Vibrationally resolved photoelectron asymmetry parameter for H_2. Experiment: ●, present data, taken at NBS; ■, present data, taken at Daresbury Laboratory; ◈, Poliakoff *et al.*, Ref. 23; ⊗, Katsumata *et al.*, Ref. 17; ⧗, Kreile and Schweig, Ref. 20; ⊠, Ruf *et al.*, Ref. 24, as deduced by Hara *et al.*, Refs. 43, 44, and 47; ⧄, Pollard *et al.*, Ref. 22, as deduced by Hara *et al.*, Refs. 43, 44, and 47; ⊕, Carlson and Jonas, Ref. 15. Theory: — — —, Itikawa, Ref. 33; ———, Hara *et al.*, Refs. 43, 44, and 47; ○, Tennyson *et al.*, Ref. 46; ◇, Raoult *et al.*, Ref. 10; ▽, Itikawa *et al.*, Ref. 39.

Fig. 1 is $\langle\beta_{\mathrm{av}}\rangle = 1.79$, whereas the average of the best single-channel calculations is $\langle\beta_{\mathrm{av}}\rangle \sim 1.92$. The data move close to the preferred theoretical values near $h\nu = 22.5$ and 30 eV, but are lower elsewhere. Hence, we are led to conclude that the persistent difference between theory and experiment is reinforced by the results reported here. This same gross behavior can be seen in Fig. 2, albeit with larger scatter in the data.

Regarding energy dependence, there does appear to be a modulation of both β_{av} and $\beta(v)$ throughout this spectral range. This modulation is not well defined, due to the lack of precision in the data. In fact, its magnitude is often only slightly more than the combined error bars of nearby points. For instance, multiple measurements at $h\nu = 27$, 28, and 35 eV often produce total uncertainty ranges of 0.3 or more β units, which is approaching the amplitude of the modulation in many cases. Also, the structure at $h\nu = 34.5$ eV hinges on a single datum and must be considered very tentative. Nevertheless, a rough pattern does emerge from the data. The low-energy NBS data show a gradual rise at threshold and a broad maximum near $h\nu = 23$ eV. These data then join smoothly with the higher-energy data, taken at Daresbury, which exhibit two minima, one on either side of a broad maximum near $h\nu=30$ eV. The structure is damped in the vibrationally averaged β_{av} in Fig. 1, and appears more pronounced in the statistically more uncertain vibrational components $\beta(v)$. There are apparent differences in the various $\beta(v)$ curves, but the present data are not of sufficient quality to establish a systematic v dependence. Certainly, no major qualitative v dependence is observed.

From the observed gross spectral average of $\langle\beta_{av}\rangle\sim1.79$, and the wavelength dependence, we conclude that the body of existing data departs from the best single-channel-model calculations, and that this model is therefore missing some essential physics. A possible contributing mechanism is suggested by recent calculations by Raseev[41,42] and by Tennyson *et al.*[46] who have included interactions of the direct ionization process with doubly excited states of H_2 converging to repulsive ionic states of $H_2{}^+$. These calculations have heretofore been restricted to a few values of the internuclear distance R. A representative result by Raseev[41,42] is shown by a solid curve in Fig. 1. This calculation was carried out at $R=1.7a_0$ and includes the interaction with doubly excited ${}^1\Pi_u$ and ${}^1\Sigma_u$ states of H_2 having the configurations $2p\sigma_u2s\sigma_g$, $2p\sigma_u3s\sigma_g$, and $2p\sigma_u3d\pi_g$. Clearly the resulting β_{av} exhibits strong dips at the resonance positions with different shapes and widths. Moreover, the positions and shapes of these features are sensitive functions of R. Indeed, the resonance positions are observed[42] to span nearly all of the spectral range discussed here as R varies over the range $1.2a_0<R<2.4a_0$, which spans the combined ground-state vibrational motions of H_2 and $H_2{}^+$. Ranges of R covering higher vibrational states of $H_2{}^+$ would produce even larger spectral shifts for the resonant features. In addition to the sharp dips, the curve in Fig. 1 shows that the resonance profiles can depress the value of β_{av} from the independent channel value over significant spectral ranges. Naturally sharp features will be smeared out when R dependence is adiabatically incorporated into the calculation. Therefore, it is possible that this mechanism may be responsible, in part, for the lower magnitudes and energy dependence of β_{av} and $\beta(v)$ observed in this work.

This conclusion is very pleasing, yet tentative, requiring further work on both the theoretical and experimental side. On the theory side there is a need for channel interaction calculations to incorporate the dependence on internuclear separation in order to examine how these resonance effects are affected by vibrational motion and, simultaneously, to produce vibrationally resolved results. This seems to be the most pressing step at this time. Also, only the lowest one or two members of selected channels of doubly excited states have been considered, a limitation it would be good to remove or at least critically assess. Dependence on other features of the calculations, e.g., partial-wave expansions, quality of initial- and final-state wave functions, have been studied fairly extensively. On the experimental side, it remains necessary to improve the quality of data for this difficult but important measurement. Continued efforts to develop a clearer picture of the wavelength dependence reported here will require an improved control of polarization, angular calibration standards, data quality, and background treatment, each of which has great leverage in achieving high-precision results for systems with high asymmetries, low cross sections, etc. as discussed in Sec. II.

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