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Observation of UV-Fluorescence of the HeH-Molecule

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Abstract

This letter reports on the first spectroscopic detection of HeH, the simplest excimer molecule that can exist. HeH* is produced in electronically excited states in reactions between He and H_2 excited selectively by synchrotron radiation into the C $^1\Pi_u$ (v' ≥ 1) or B $^1\Sigma_u^+$ (v' ≥ 11) state. HeH* emits a broad characteristic fluorescence continuum between 200 and 400 nm which is attributed to B $^2\Pi \rightarrow X\ ^2\Sigma^+$. Similar results are obtained for all other rare gas hydrides.

1. Introduction

HeH is one of the smallest molecular systems. Due to its simple electronic configuration it attracts theoretical interest since many years[1,2]. Its ground state is strongly repulsive, but already 20 years ago, a detailed molecular orbital calculation predicted that many strongly bound excited states exist[2]. The main contribution to the bond is the polarization of the He atom by the H^+ core which gets very efficient if H penetrates the electronic cloud of He. For the lowest excited states, A $^2\Sigma^+$ and B $^2\Pi$, a binding energy of ~ 2 eV was predicted[2]. In the meantime, more sophisticated ab initio calculations underlined the existence of bound excited states[1].

To the best of our knowledge, up to now no experimental evidence of bound excited states of HeH was found. The same is true for the other rare gas hydrides with the only exception of ArH. Johns[3] reported on infrared fluorescence bands in a gas discharge which he ascribed to a $^2\Pi \rightarrow {}^2\Sigma^+$ transition of ArH. Very recently, Sadeghi et al.[4] assigned a fluorescence continuum in the UV region which is generated in reactive collisions of thermal Ar metastables with H_2 to ArH emission.

In this paper, we report on the first spectroscopic proof of the existence of rather long lived excited states of HeH. They lead to broad UV bound-free fluorescence continua terminating at X $^2\Sigma^+$. Similar results were also obtained for the other rare gas hydrides and will be published elsewhere[5]. Here we concentrate on HeH which is most important from the theoretical point of view, especially in view of the various calculations of H_2 + He surfaces and interactions.

2. Experiment

Electronically excited HeH molecules were obtained from elementary reactions of the type

$$\mathrm{He} + \mathrm{H}_2^* \rightarrow \mathrm{HeH}^* + \mathrm{H} \qquad (1)$$

in H_2 doped He. The pressures ranged between 0 and 10 torr (H_2) and 1 and 20 torr (He). Primary excitation of H_2 was performed optically with synchrotron radiation at the experimental set-up SUPERLUMI at HASYLAB which is described in detail elsewhere[6,7]. The spectral resolution of excitation was sufficiently high for rotationally selective excitation of H_2 (0.007 nm $< \Delta\lambda < 0.25$ nm).

In fig. 1, calculated potential curves of HeH [1] and those H_2 potential curves[8] which are important in view of this paper are plotted in a common energy scale. Assuming optical excitation, it immediately follows from fig. 1, that H_2 has to be excited either into high vibrational levels of the B state or into the C state. Therefore, excitation wavelengths below the LiF cut-off are required. For this reason, the gas cell used was not equipped with the usual LiF entrance window for the exciting light but with a thin In window (thickness 100 nm).

The fluorescence light was analysed at right angle to the exciting beam either with a high flux toroidal grating VUV monochromator[7] or another high flux monochromator for the UV and visible spectral range. The band pass of analysis (fwhm) is given in the respective figures.

The data were recorded with single photon counting techniques. Exploiting the unique time structure of synchrotron radiation (at HASYLAB: excitation pulses with a fwhm of ~ 150 ps at a repetition rate of 4 MHz during our experiment) fluorescence was recorded only within a short time window (~ 10 ns) immediately following the excitation pulses. The length of the time window roughly corresponds to the lifetime of the emitting state. In this way, the signal-to-noise ratio was improved substantially.

3. Results and Discussion

3.1 Fluorescence spectra and excitation spectra

Fig. 2 yields fluorescence spectra which are observed following selective excitation of v' = 2, 3, 4 of the C $^1\Pi_u$ state of H_2 in a mixture of .3 torr H_2 and 20 torr He. The spectra are corrected for the spectral characteristics of the monochromator and the detector.

For the lowest excitation energy, a broad, asymmetric continuum is observed with a maximum at 235 nm. With increasing excitation energy, the continuum further broadens and shifts to shorter wavelengths. For v' = 4 excitation it already reaches the cut-off of the transmission of the monochromator used (dashed part of the curves). The statistics of the curves suffer from the low counting rates (~ 10 ... 30 cps).

The observed spectra are ascribed to the decay of HeH created via (1). Among the two HeH excited states (A $^2\Sigma^+$ and B $^2\Pi$) which have to be taken into consideration as emitting states (see fig. 1), we prefer to ascribe the emission to B $^2\Pi \rightarrow$ X $^2\Sigma^+$ transitions. Johns[3] showed that the A $^2\Sigma^+$ state of ArH strongly predissociates. Due to the great similarities among the rare gas hydride electronic structure the same may hold also for HeH (predissociation of A $^2\Sigma^+$ into the repulsive ground state is fully allowed). Further details of the fluorescence spectra will be discussed below.

It must be pointed out very clearly, that in the wavelength range of the observed emission, in, e.g., gas discharges, the well known a $^3\Sigma_g^+ \rightarrow$ b $^3\Sigma_u^+$ continuum of H_2 is emitted, too[9]. Though optical excitation of H_2 in the H_2/He mixtures used primarily terminates at ungerade singlet states, one has to take into consideration collision induced intersystem crossing (ISC), leading to the population of the H_2 a $^3\Sigma_g^+$ state and its subsequent emission. The results presented now, however, strongly support our assingment of the observed fluorescence continuum to HeH.

In fig. 3 we present excitation spectra of the fluorescence emitted in the wavelength interval 210 - 350 nm. The lower curve was obtained from 5 torr H_2 without He. All the observed lines can be ascribed to N_2 transitions. The strongest signal at 95.8 nm, e.g., is due to N_2 X $^1\Sigma_g^+ \rightarrow C_4'(0)$ $^1\Sigma_u^+$ excitation[10]. Though the contamination of H_2 by N_2 was small (< 200 ppm), the

N_2 excitation lines show up because they lead to the allowed $C'\,^1\Sigma_u^+ \rightarrow a\,^1\Sigma_g^+$ and $b\,^1\Pi_u \rightarrow a\,^1\Sigma_g^+$ transitions which emit within the wavelength interval of observation[10]. Following primary excitation of H_2 itself, no emission between 210 and 350 nm was observed. This shows that even at the relatively high gas pressure used, the collision induced intersystem crossing can be neglected (pure H_2).

In the presence of He (upper curve; 20 torr He + 0.3 torr H_2) clearly the rotational bands of the $C\,^1\Pi_u$ state ($v' = 2, 3, 4, 5$; $v' = 1$ very weak) are resolved. No signal is observed under $v' = 0$ excitation. Additionally to the C state, rotational bands of the B state ($v' \geq 11$) are observed, however with smaller intensity. For comparison purposes, various band head wavelengths of the B and the C state are marked in fig. 3 [8].

The excitation spectrum clearly yields a threshold for the population of the emitting state. In the crudest approximation one might take the energy of $v' = 1$ of the H_2 C-state as threshold energy. It correlates well with the theoretical prediction for the energetical threshold of the elementary reaction (1) which can be deduced from the calculated potential curves[1]. This is a strong support for our assignment of the observed emission. Concerning the other rare gas/H_2 systems, they all yield a clear onset behaviour of rare gas hydride emission, too[5]. The individual onsets, however, are markedly different in agreement with the different binding energies of the emitting states involved. Concerning the H_2/Ar system we want to point out that the threshold of the emission ascribed to the ArH molecule is significantly below the minimum of the $H_2\ a\,^3\Sigma_g^+$ state[5], in agreement with the data of Sadeghi et al.[4].

From the observed onsets and the well known dissociation limits of the rare gas hydride $B\,^2\Pi$ states (He ^1S + H* ^2P) the binding energies of the B-states can be estimated. Results are given in table 1 and compared with theoretical predictions. Concerning HeH, two values, namely $D_e = 1.94$ eV[2] and 2.2 eV[1] are available (well depths). The experimental value $D_0 = (2.05 \pm 0.1)$ eV (dissociation energy of the B-state) is in good agreement.

Now we may comment on the spectral distribution of HeH emission for different excitation energies (fig. 2). Following H_2 C ($v' = 2$) excitation near to the threshold, in the subsequent elementary reaction (1) predominantly HeH B ($v' = 0$) molecules are produced. The decay of such vibrationally relaxed molecules into a strongly repulsive final state leads to a broad single centered band in agreement with observation. We should also mention, that fluorescence from the energetically nearest level $v' = 3$ of the H_2-$a\,^3\Sigma_g^+$ state looks completely different[9].

With increasing excitation energy, higher vibrational levels of the HeH B-state may be populated. This explains the observed broadening. The observed shift to shorter wavelengths is ascribed to an effect of FC-factors and the ν^3-dependence of the transition probabilities.

3.2 Cross section of HeH formation

Fig. 4 shows a fluorescence spectrum of 10 torr He doped with 0.3 torr H_2 including the VUV spectral range. The excitation wavelength of 96.5 nm ($\Delta\lambda$ = 0.25 nm) corresponds to the strongest rotational line ($J' = 2$) of H_2 C ($v' = 2$). However, simultaneously also $J' < 2$ of H_2 C ($v' = 2$) and $J' = 2, 3$ of H_2 B ($v' = 12$) are excited with the chosen bandwidth of excitation. Due to the low counting rates, the spectral resolution of the fluorescence spectrum could not be improved to resolve details of the VUV H_2 emission. Both bound-bound C → X transitions around 120 nm and bound-free fluorescence of the B-state around 160 nm, emitted at large internuclear distances, are observed[11] (curve (a)).

The strong lines in curve (a) around 240 and 280 nm are second order light. Using a filter of air (curve (b)) they are absent. Then only the HeH continuum is observed. It is interesting to note that in the second order spectrum, due to the doubled spectral resolution, the transition H_2 C ($v' = 2$) → X ($v'' = 5, 6$) are clearly resolved whereas they merge one into each other in first order.

The intensity ratio of H_2 and HeH fluorescence gives a rough estimate of the total cross section, σ_r, of the reaction

$$H_2\ C\,^1\Pi_u\ (v' = 2) + \mathrm{He} \rightarrow \mathrm{HeH}\ B\,^2\Pi + \mathrm{H} \qquad (2)$$

The FC-factors of H_2 C → X and B → X transitions are known well enough[12] to calculate the total H_2 fluorescence intensity from the observed part of the spectrum. Neglecting additional quenching of H_2 and HeH fluorescence (which is justified in view of the low gas pressures used), the ratio of the fluorescence intensitites is then given by

$$I_{HeH}/I_{H_2} = \Gamma_f/\Gamma_{rad} \qquad (3)$$

Γ_f is the rate of formation of HeH, Γ_{rad} is the radiative decay rate of the primarily excited H_2 molecule which was measured separately. Γ_f obtained from (3) is finally converted into σ_f using classical kinetic expressions. As a result we obtain $\sigma_f = (1.6 \pm 1)$ Å^2 for the C (v' = 2) state. This is an average value concerning the rotational quantum number (J' $\leq$ 3). It is ascribed to the C-state, because the C-state rotational bands in the excitation spectrum are much stronger than the B state rotational bands (especially true for C (v' = 2) compared with B (v' = 12).

For C (v' = 1) the cross section seems to be much smaller. This may be explained in the following way. A more rigorous evaluation of the threshold for the elementary reaction (2) has to take into account also endothermic reactions of particles in the tail of the Maxwellian velocity distribution and would place the energetic threshold somewhere between v' = 1 and v' = 2. However, it is not the purpose of this paper to discuss these details.

Though the estimate of σ_f is very rough, it is included in this paper, because its order of magnitude which is beyond doubt, is important to rule out that the observed fluorescence around 235 nm is due to emission of the H_2 (a $^3\Sigma_g^+$) state. For this purpose we now estimate the cross section for the reaction

$$H_2\ C\ ^1\Pi_u\ (v' = 2) + He \rightarrow H_2\ a\ ^3\Sigma_g^+ + He \qquad (4)$$

From the H_2 potential curves (fig. 1) it follows that collision induced ISC of C (v' = 2) and a ($^3\Sigma_g^+$) most probably populates v' = 3 of the a-state due to the small energetic distance. This is also reasonable in view of calculated potential surfaces of the HD + He system[13]. In their paper, Römelt et al. especially present results for He + HD (C $^1\Pi_u$) and of He + HD (a $^3\Sigma_g^+$), both for v' = 0 and different geometries[13]. By adding the known vibrational energies we obtain the corresponding curves for v' = 2 (C-state) and v' = 3 (a-state). For the collinear geometry, these potential curves are shown in the right part of fig. 1. They may be a good estimate for the He + H_2 system. The potential curves cross one each other at a distance of about 3 Å between the He atom and the center of H_2.

During the collision, the g/u symmetry of the dissociation limits is destroyed Then spin-orbit and spin-spin interaction leads to a perturbation in the crossing region, and the resulting adiabatic potential curves yield an energy gap. As an upper limit we tentatively took twice the spin-orbit interaction energy, E_{so} = 0.3 cm^{-1} [14] of the atoms.

The probability for the C → a transition during one passage of the crossing region is estimated with the Landau-Zener probability[15]

$$p = 1 - \exp\left\{- \frac{4\pi^2 \Delta E^2}{hv|\Delta F|}\right\} \qquad (5)$$

2ΔE is the width of the gap, ΔF is the difference of the gradients of the diabatic potential curves, and v is the relative velocity of the particles in the crossing region. With 2ΔE = 0.6 cm^{-1}, $|\Delta F| = 1 \times 10^{-9}$N and v = 2 × 10^3 ... 10^{4}ms^{-1} we obtain p = 10^{-4} ... 10^{-5}.

This value must be compared with the yet unknown probability, p_R, of reaction (2). As an estimate, we take the calculated probability of the direct reaction $H_2^+ + He \rightarrow HeH^+ + H$, which is about 10^{-1} ... 5 × 10^{-1} [16]. The estimate is justified because the potential surfaces of H_2 (C) + He and H_2^+ + He are very similar (both the C state of H_2 and the B state of HeH are nearly parallel to the ionic limits, see fig. 1). It is obvious, that the ISC probability cannot compete with the probability of the chemical reaction. It is interesting to note that the cross section of $H_2^+ + He \rightarrow HeH^+ + He$, $\sigma \approx 1$ Å^2 [17], is similar to our result, $\sigma_f = 1.6$ Å^2, ascribed to H_2 (C) + He → HeH + H.

In conclusion, the UV fluorescence continuum observed following H_2^* + He collision is undoubtedly due to the decay of HeH and thus the first experimental proof of the existence of this strange molecule. The continuum cannot stem from the a-state of H_2 populated during the collision for the following reasons,

(i) the observed threshold in the excitation spectrum agrees well with the energetic threshold for HeH (B) formation,

(ii) the observed thresholds for the fluorescence continua of the rare gas hydrides are rare gas specific[5], which would be obscure for the ISC process,

(iii) in Ar/H_2 systems, the threshold is well below the minimum of the H_2 a-state, and

(iv) the estimates of the probabilities for the ISC process and the chemical reaction differ by several orders of magnitude in favour of HeH formation.

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Figure Captions

Figure 1 Potential curves of selected states of H_2, HeH and HeH_2. Excitation to C $^1\Pi_u$, v' = 2 and resulting fluorescence from HeH B $^2\Pi \rightarrow X\ ^2\Sigma^+$ are indicated by arrows. Note the change in the energy scale. Data are taken from Refs. 8, 1, and 13.

Figure 2 Fluorescence of HeH (B $^2\Pi \rightarrow X\ ^2\Sigma^+$) for different excitations into H_2 C $^1\Pi_u$. The spectra are corrected for the spectral response of the system, below 200 nm they are uncertain due to the cut-off of the response function.

Figure 3 Excitation spectrum of near UV-fluorescence (210 nm - 350 nm) of pure H_2 (5 Torr) and a mixture of 0.3 Torr H_2 and 20 Torr He. The lines in pure H_2 are due to N_2 impurities (see text).

Figure 4 Fluorescence of a mixture of 0.3 Torr H_2 and 10 Torr He excited at 96.5 nm (B $^1\Sigma_u^+$, v' = 12, C $^1\Pi_u$, v' = 2). The strong lines between 200 nm and 300 nm in the upper part are second order lines. The lower spectrum (b) is measured with air as a short wavelength cut-off filter and displays the continuum of HeH without second order lines of H_2 emission.

Table 1

Dissociation energies (D_o) of rare gas hydride B $^2\Pi$ states (terminating at H* (^2P)) in comparison with calculated binding energies (D_e); a) from Ref. 1, b) from Ref. 2.

	HeH	NeH	ArH	KrH	XeH
D_o [eV] this work	2.05	1.80	2.93	2.9	≥ 3.6
D_e [eV] theory	2.20[a] 1.94[b]	1.67[a]	2.75[a]		

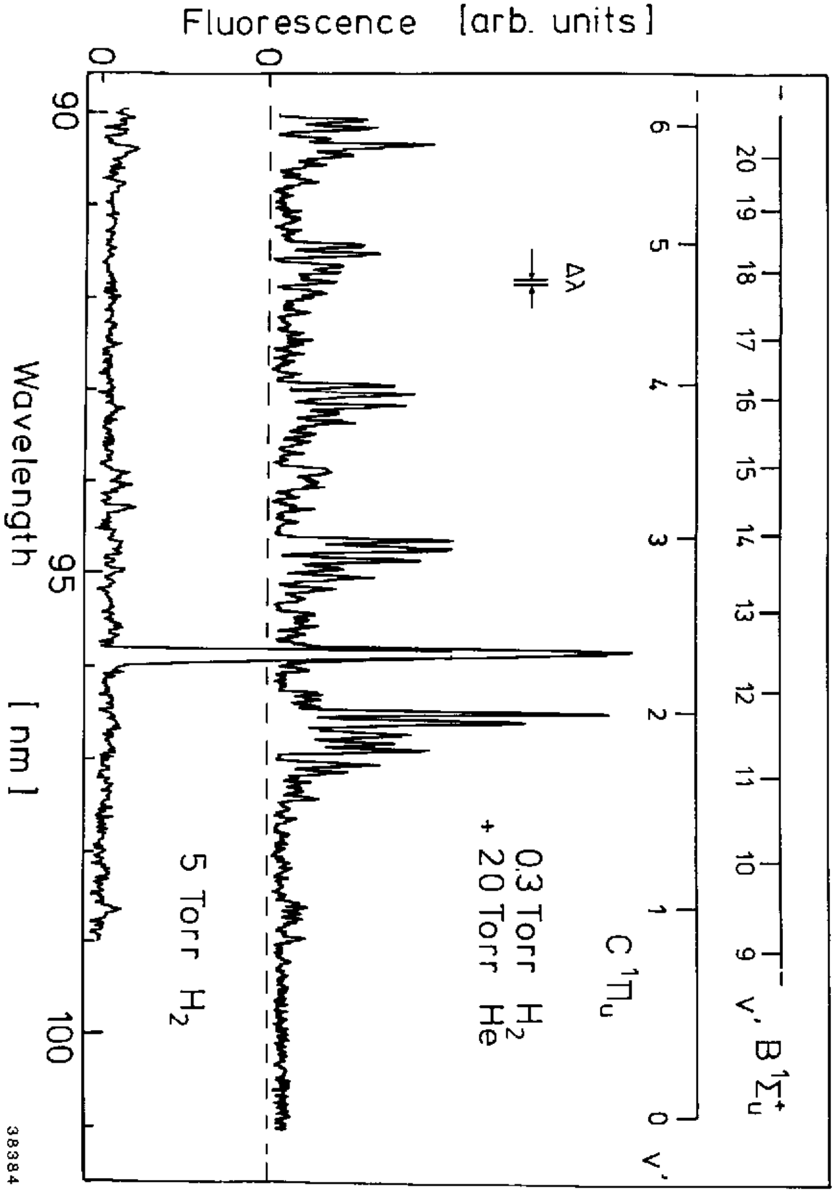

Fig. 3

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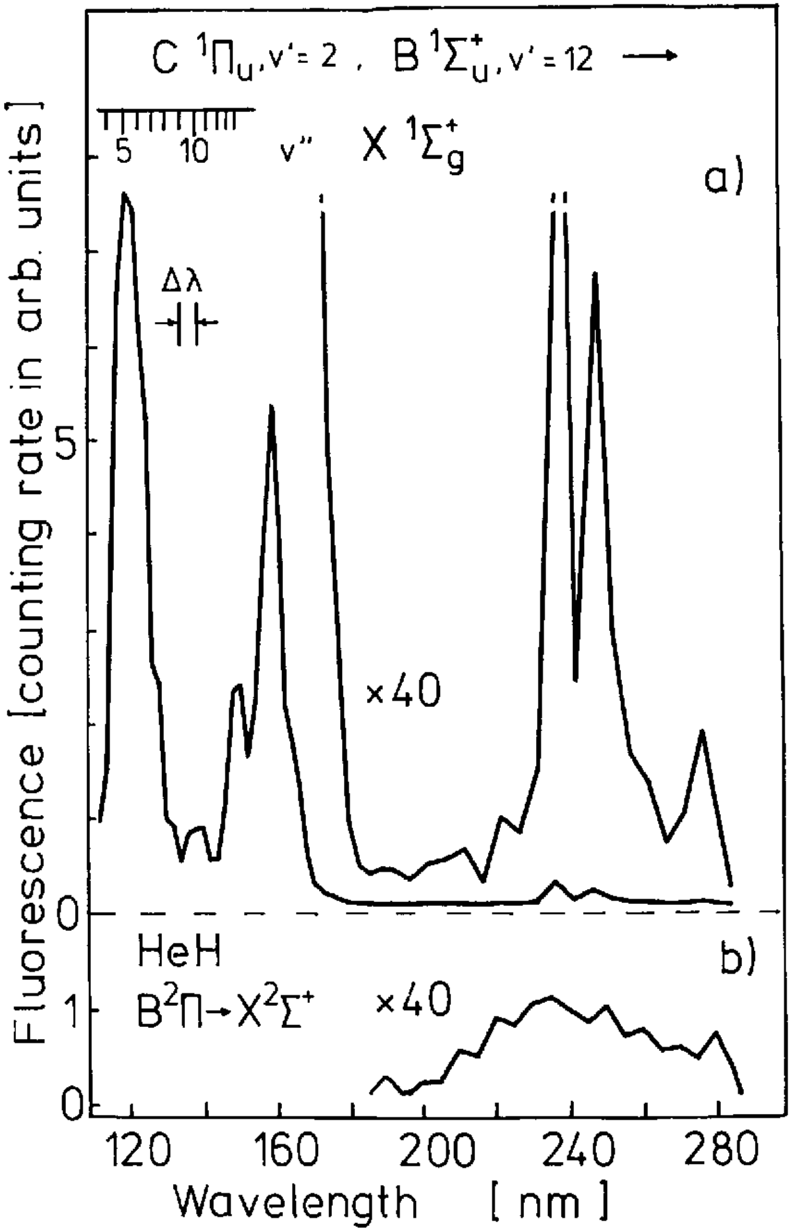

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Fig. 4

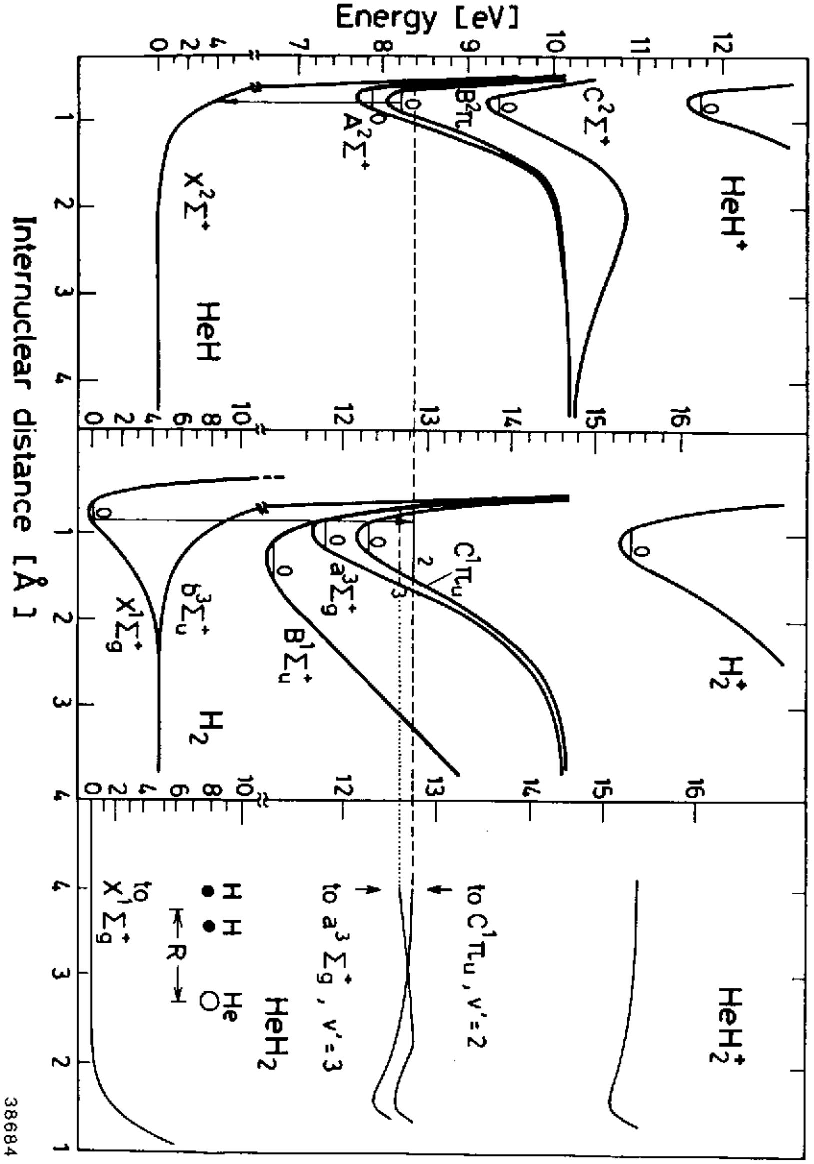

Fig. 1

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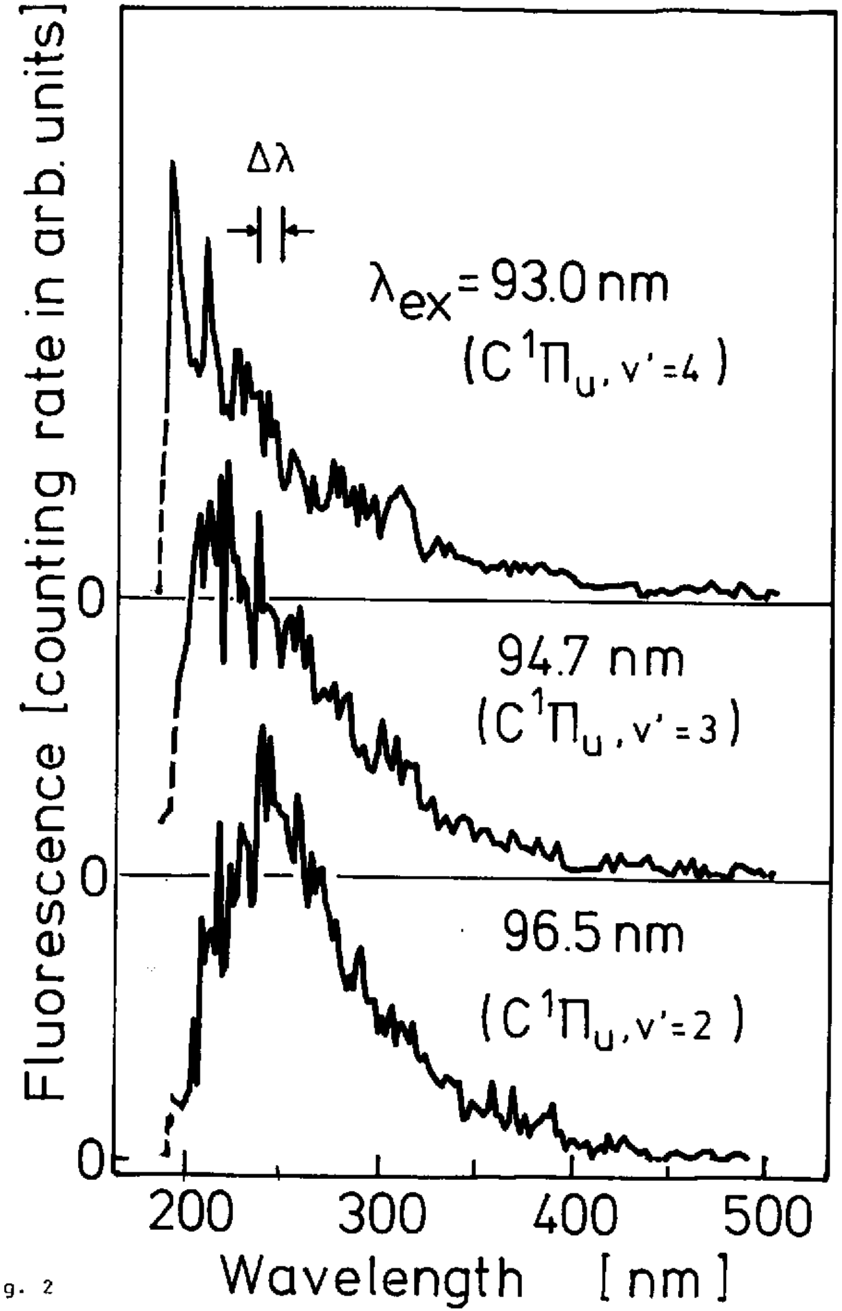

Fig. 2

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