Ultraviolet continua of He_2^+

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Two previously unclassified helium optical emission continua, seen in arc and other discharges, are found to result from a transition between excited states of He_2^+. *Ab initio* potential curves are calculated for the states involved, and semiempirical spontaneous emission spectra are obtained that fit experimental data. The corresponding cross section for stimulated emission suggests the possibility of a laser with a tuning range of 2500 to 10 000 Å peaking at ~6000 Å. A broadband emission at ~6050 Å may be evidence of laser gain.

Most ultraviolet continua of helium molecules result from electronic He_2 transitions in the relatively cool conditions of a pulsed discharge afterglow.[1] Two continua that occur *during* a discharge are explained here in terms of vibrational bands of a He_2^+ electronic transition. As this transition has a bound upper state and an unbound lower state, there is a population inversion, and the possibility of a new kind of laser.

Huffman, Tanaka, and Larrabee[2] generated an intense continuum, 1050–4000 Å, using a self-triggering helium discharge (100–800 Torr). A capacitor (0.06 μF) connected directly across a 100-mm-long capillary arc[3] lamp discharged repetitively as a power supply charged it towards 10 kV. The continuum became observable only at pressures greater than 100 Torr. By 200 Torr it was brighter than the Hopfield[4] continuum, becoming the dominant emission. With increasing pressure, the intensity of the He II lines also increased, indicating increased temperature. The existence of He II lines in this arc and not in the instances discussed below indicate temperatures significantly higher in the long pulsed arc of Huffman. The purity conditions required for the Hopfield continuum could be relaxed for Huffman's continuum.[2] Insensitivity to impurity is consistent with the simple association formation reaction proposed later. The $2\,^3S$-$n\,^3P$ series in the published[2] spectrum allows an estimation of the electron density. The Inglis-Teller relation[5] gives a value of $3.3^{+6.7}_{-2.1}\times10^{16}$ cm^{-3} at 600 Torr. Huffman, Tanaka, and Larrabee suggested that the most likely cause of the continuum was He_2^+ but in the absence of potential curves reached no definitive conclusion.

Under the same conditions as those for the main continuum, Huffman, Tanaka, and Larrabee[2] observed a single broad emission band at ~6050 Å (photon energy of 2 eV), the width of which was not reported. This emission increases in intensity with pressure as does Huffman's continuum. No explanation has been offered for the origin of this band. The neutral atomic and molecular emissions are absent, or diminishing in intensity, rendering an explanation in terms of these species difficult. Inspection of the potential curves[6] for spontaneous transitions among excited states of He_2^+ provides no obvious explanation of this broad visible band.

Simon and Rodgers[7] examined a short arc which had the same continuum features as the long arc of Huffman, Tanaka, and Larrabee.[2] In a published[7] photographic plate the continuum is clearly visible. The 5-mm-long discharge was powered by welding supplies that generated 250 A dc. The existence of this continuum in steady-state conditions indicates that the molecular state responsible is continuously produced—a prerequisite for a continuously operating laser. The arc was imaged onto the slit of a monochromator and then onto a photographic plate enabling the radial extent of the light to be determined. The continuum was confined to the central region of the discharge. Simon and Rodgers[7] found the central region to have a temperature of 4000–8000 K, and electron density of $1.2^{+2.1}_{-0.2}\times10^{16}$ cm^{-3} at 850 Torr and 100 A.

In a water-cooled lamp powered by the transformer for a commercial advertising light (10–50 mA) at pressures greater than 100 Torr, Tanaka observed a different continuum,[8] but only a qualitative description of the emission is available. The weak featureless continuum extends from ~2100 to 6500 Å and beyond with a flat maximum near 4000 Å. With increased pressure the intensity of the continuum was found to be enhanced at the expense of atomic line and molecular band emissions.

The main aim of this work was to find a satisfactory model for Huffman's continuum.[2] Somewhat unexpectedly, the analysis yielded an explanation for Tanaka's continuum[8] as well. Earlier it was thought, due to the cool, low-power, conditions of Tanaka's continuum, that a different mechanism, possibly involving trimers was responsible for this very broad featureless continuum.[1]

As for the Hopfield emission, Huffman's continuum results from a bound to unbound state transition. Unlike the Hopfield continuum, however, the spectrum maintains the same shape over a range of pressures. This suggests that, in contrast to the Hopfield case, there is only one upper state involved in this transition.

Huffman's spectrum has a range from 1050 to 4000 Å (11.8–3 eV). Inspection of the potentials[6,9,10] (Fig. 1) for He_2, He_2^+, and He_2^{2+} reveals that the only lower state for which the transitions would have the required energy range is $He_2^+(A\,^2\Sigma_g^+)$. The selection rules for allowed

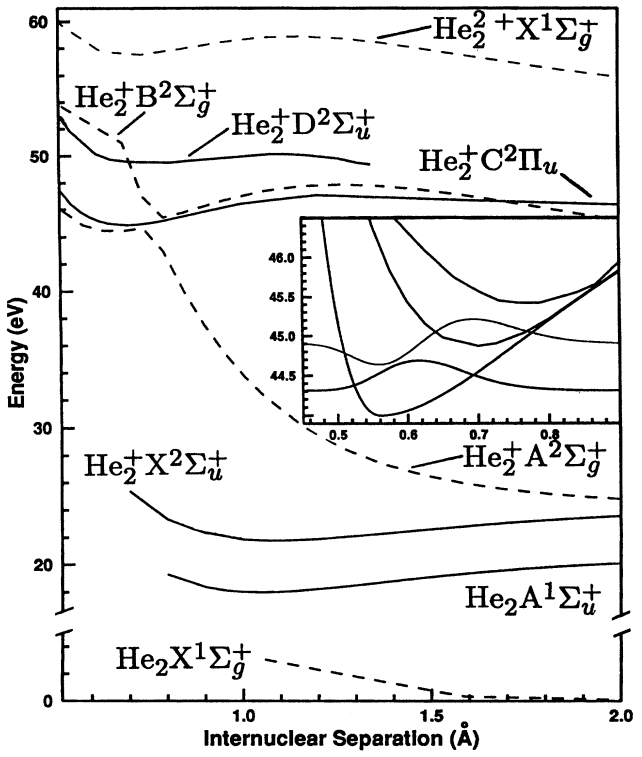

FIG. 1. *Ab initio* potential curves. The states of even inversion symmetry are indicated by dashed lines, those of odd by solid lines. The sources for the curves from top to bottom at $R=1$ Å are as follows: Ref. 11, this work, Refs. 11, 6, 11, 11, 12, and 13, respectively. Inset: potential curves for the $C\,^2\Pi_u$ state. The upper curve is from Ref. 6. The middle curve was calculated using Blint's basis but with a full CI. The lowest curve is the semiempirical curve. Also shown are the wave functions of vibrational levels $v=0$ and 1.

transitions restrict the upper states to those with uneven inversion symmetry. The energy of the emitted light imposes further restrictions, leaving only two possible upper states: $D\,^2\Sigma_u^+$ formed from He($2\,^3S$) and He^+; and $C\,^2\Pi_u$ formed from He($2\,^3P$) and He^+. *Ab initio* potential curves were calculated for both these symmetries and the spectra resulting from a transition to the $A\,^2\Sigma_g^+$ state determined.

Blint's potential curves[6] were further improved through a full configuration interaction (CI) calculation[14] using his basis set. The results for the $D\,^2\Sigma_u^+$ and $C\,^2\Pi_u$ states are shown in Fig. 1 which emphasizes appreciable lowering of his $C\,^2\Pi_u$ potential curve at internuclear separations $R<0.8$ Å. Spontaneous emission spectra were calculated from the potential curves using a coupled Schrödinger equation technique,[15] necessary to account for an avoided crossing of the $A\,^2\Sigma_g^+$ and $B\,^2\Sigma_g^+$ states at 45 eV, with a coupling[6] of 0.78 eV. This technique uses diabatic potentials and coupling which are calculable from the adiabatic curves generated by the *ab initio* calculation. The diabatic dipole transition moments were assumed to be independent of R over a range of 0.65–0.85 Å.

The nature of the sodium salicylate scintillator, used at the exit slit of the monochromator,[2] is important for both interpretation and calculation of the spectrum. Such a scintillator has practically constant quantum efficiency over the wavelength range of the spectrum.[16] Hence the vertical scale of the spectrum given in Ref. 2 is proportional to the number of photons incident on the detector. Accordingly, the calculation contains a wavelength factor λ^{-5}. An additional signal is expected above 3500 Å as the light scatters through the scintillator and can be detected by the photomultiplier.[17]

The upper state can be identified by comparing the theoretical and experimental results. The $D\,^2\Sigma_u^+$ is not the upper state because the calculated spectrum predicts for Huffman's smooth continuum, Fano minima caused by quantum-mechanical interference between the two coupled lower $A\,^2\Sigma_g^+$ and $B\,^2\Sigma_g^+$ states. The $C\,^2\Pi_u$ state undergoes transitions to below avoided potential crossing of the A and $B\,^2\Sigma_g^+$ generating a smooth continuum. The $He_2^+(C\,^2\Pi_u - A\,^2\Sigma_g^+)$ spectrum most closely parallels the experimental observations. Thus this transition is the likely origin of Huffman's continuum.[2]

The model used to identify the transition only included the $v=0$ level of the *ab initio* $C\,^2\Pi_u$ potential curve. This is, admittedly, simplistic as the emission is known to be from a gas above 4000 K and hence will have contributions from higher vibrational levels. It is possible that Tanaka's continuum is caused by transitions from the $v=0$ vibrational level and that Huffman's continuum is from higher vibrational levels. A semiempirical curve (Fig. 1 inset) was developed to model the experimental results (quantitative spectrum of Huffman, Tanaka, and Larrabee[2] and qualitative description of Tanaka and coworkers[8]). As there are no other upper states lower in energy than $C\,^2\Pi_u$ the lowering of the semiempirical curve adds no ambiguity to the assignation. The accuracy of this curve is limited by the accuracy of the $He_2^+(A\,^2\Sigma_g^+)$ potential curve,[11] the approximation that the dipole transition moment is constant, and uncertainties in Huffman's data like grating and scintillator efficiency.

The room-temperature spectrum, so obtained, indeed successfully describes the major features of Tanaka's continuum (Fig. 2). At higher temperatures, radiation from the $v=1$ level dominates because of a greater Franck-Condon overlap and the λ^{-5} factor in the radiation rate equation. The theoretical spectrum fits Huffman's continuum for all temperatures ≥ 4000 K. Tunneling through the $C\,^2\Pi_u$ state potential barrier and the influence of a second minimum [0.3 eV beneath the dissociation energy of 45.4 eV at $R=2.9$ Å (Ref. 6)] may explain the lack of radiation from levels higher than $v=1$. The matter is open until better potential curves are available. An attempt was made to explain the inflection in Huffman's continuum[2] near 2000 Å in terms of transitions from $v>1$ was unsuccessful due to the spectral broadness of each vibrational contribution.

Comparison of the integrated area of the continuum with that of the line structure[2] indicates that a substantial fraction ($\gg 50\%$) of the radiant energy of the discharge is released in this transition. In a helium discharge, ener-

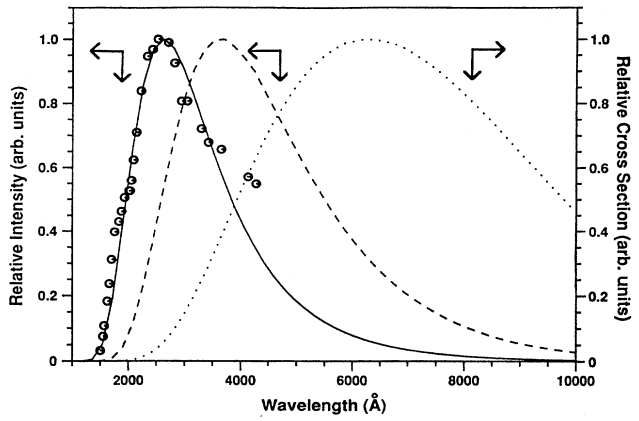

FIG. 2. Relative experimental and semiempirical rates. Circles: continuum of Huffman, Tanaka, and Larrabee (Ref. 2). Solid curve: calculated, temperature greater than 4000 K. Dashed curve: calculated, temperature equal to 300 K. Dotted curve: stimulated emission cross section, $v=0$.

gy is stored in lower atomic excited states, either as metastable states or as resonantly trapped radiation. This energy is liberated when the excited states form molecules, achieve new symmetries, and can radiate.

A three-body momentum transfer collision is required for a $C\,^2\Pi_u$ molecule, consisting of He^+ and $He(2\,^3P)$, to drop into a bound state,

$$He+He^+ +He(2\,^3P)\rightarrow He+He_2^+(C\,^2\Pi_u)\ , \tag{1}$$

$$He_2^+(C\,^2\Pi_u)\rightarrow He_2^+(A\,^2\Sigma_u^+)+\nu\rightarrow He+He^+ +\nu\ . \tag{2}$$

This state has a calculated[6] potential barrier of 1.6 eV, the lowest for any of the excited doublet states, making it the most likely reaction. Collisional relaxation lowers the molecule through the vibrational levels swinging the equilibrium towards the formation of the molecule. The association of $He(2\,^3S)$ and He^+ in low-energy discharges to form $He_2^+(^4\Sigma_u^+)$ in preference to the ground-state dimer ion is a similar type of reaction.[18] In overview, the conditions of an arc may be seen as facilitating catalytic conversion by He^+ of $He(2\,^3P)$ to $He(1\,^1S)$ and a photon, explaining the dominance of the continuum radiation.

Recombination of He_2^{2+} and subsequent radiative decay may also have a role in creation of $C\,^2\Pi_u$ state. Ground state He_2^{2+}, formed by the collision of two helium ions, requires a threshold energy[10] of 3.5 eV to overcome its potential barrier. If such dimer di-cations exist, they would form the $C\,^2\Pi_u$ state upon recombination because of the similar ranges over which the two molecules are bound, and the high electron densities favoring the formation of lower excited states. (For an example involving He_2, see Ref. 19.)

Simon and Rodgers[7] reported electron densities in the range $10^{16}-10^{18}$ cm^{-3} for continuous arcs at pressures of 500–5000 Torr. The high electron densities will then facilitate rapid three-body collisional recombination. Recombination of $He_2^+(X\,^2\Sigma_u^+)$ leads to the Hopfield continuum.[1] As the Hopfield continuum is only seen very weakly, it may be inferred that this state is a minor ionic species. One important reaction discussed by Bates,[20] involving the destruction of $He_2^+(X\,^2\Sigma_u^+)$ and the production of $He(2\,^3P)$, which is in turn necessary for the creation of the $C\,^2\Pi_u$ state is

$$He_2^+(X\,^2\Sigma_g^+)+He+He\rightarrow He_3^+ +He\ , \tag{3}$$

$$He_3^+ +e\rightarrow He(2\,^3P)+He+He\ . \tag{4}$$

Further investigation is required to predict the concentration of $He_2^+(C\,^2\Pi_u)$.

As the lower state in the transition is unbound there is automatically a population inversion. The spontaneous emission rate per unit wavelength, $W_{ab}(\lambda)$, is related to the stimulated-emission cross section σ_{stim} by

$$\sigma_{\text{stim}}=W_{ab}(\lambda)\frac{\lambda^4}{8\pi c}\ . \tag{5}$$

In the absence of a value for the lifetime for $He_2^+(C\,^2\Pi_u)$, only the relative magnitude of the $\sigma_{\text{stim}}(\lambda)$ can be deduced. The spontaneous emission curve for Tanaka's continuum (Fig. 2) and Eq. (5), are used to calculate the cross section for stimulated emission (Fig. 2). If the lifetime were 2 ns the cross section would be 10^{-16} cm^2 at 6050 Å. The dipole transition moment is currently being calculated in order to predict the lifetime. A possible explanation of the lone broad emission band[2] found at ~6050 Å may be laser gain. Although this would indicate very high gain for a path length of only 100 mm this proposition gains plausibility from the observation that the 6050-Å feature is near the peak in the cross section for stimulated emission and that the feature was only seen when the accompanying spontaneous emission spectrum from the C state was strong.

A He_2^+ transition has been identified which explains both Huffman's and Tanaka's continua. A laser using such a transition would be useful because of its simplicity and possible tuning range. Further theoretical analysis of the lifetime and of the population of the $C\,^2\Pi_u$ state to assess the merit of such a laser is in progress.

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