

LABORATORY DETECTION OF A MOLECULAR BAND AT $\lambda 4429$

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ABSTRACT

A fairly strong molecular absorption band at $4429.27 \pm 0.04 \text{ \AA}$, closely centered on the strongest diffuse interstellar band at $4428.9 \pm 1.4 \text{ \AA}$, has been found in a supersonic molecular beam among the products of a discharge through benzene and other hydrocarbons. This agreement in wavelength to a few parts in 10^4 strongly suggests a common carrier. The width of the laboratory band is significantly less than that of the diffuse interstellar band, but this difference may be the result of the very low rotational temperature in the supersonic beam—possibly as low as 2 K—relative to that of a weakly polar molecule in the diffuse interstellar gas (100–200 K). Several candidate carriers are discussed. Two of the more promising are the allyl cation C_3H_5^+ and the dimethylene allenyl radical C_5H_5 , both bent carbon chains that may be close enough to linear to reconcile the puzzling appearance of *P*-, *Q*-, and *R*-branches in the laboratory band with the five hydrogen atoms suggested by the observed deuterium isotopic shifts.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes

In an attempt to identify the carriers of the diffuse interstellar bands, we are systematically studying in the vicinity of the stronger bands in the laboratory by laser cavity ringdown spectroscopy (CRDS). Candidate molecules are produced in our spectrometer by an electrical discharge in the throat of a supersonic nozzle, a technique which has been used to detect over 65 new carbon chains and rings of astronomical interest (Thaddeus et al. 1998; McCarthy 1999). After trying a number of precursor gases, a fairly strong new molecular band has been found among the products of a discharge through benzene and other hydrocarbon molecules at $4429.27 \pm 0.04 \text{ \AA}$, to within the observational uncertainties the wavelength of the strongest and best known diffuse band at $4428.9 \pm 1.4 \text{ \AA}$ (Jenniskens & Désert 1993).

CRDS is a very long path laser absorption technique (O’Keefe & Deacon 1988), the long path provided by two very highly reflective mirrors ($R > 99.99\%$) coated with many dielectric layers. A brief description of the technique and our particular spectrometer is given in a recent Letter (Ball, McCarthy, & Thaddeus 1999). Laser light is generated by a YAG-pumped, pulsed dye laser (Lambda-Physik Scanmate 2E) operated at a 10 Hz repetition rate with 10 ns pulse widths. With different laser dyes, the wavelength range of the tunable radiation is from 2000 to 8000 \AA . The line width of the laser is 0.15 cm^{-1} when scanning with a grating and 0.03 cm^{-1} when scanning with an intracavity etalon. Argon lines from an optogalvanic hollow cathode lamp are used for wavelength calibration, and external etalon fringes are monitored to verify the linearity of each scan. Typical ringdown decay times are 50–100 μs , and the overall sensitivity of the spectrometer is ~ 1 part per million fractional absorption per pass.

Reactive molecules are produced in a pulsed supersonic nozzle by an electrical discharge through a stream of argon or neon containing a small amount (0.3%–1.0%) of a hydrocarbon precursor. Typically, a 400 μs gas pulse (1.5 kTorr backing pressure) passes through the discharge electrodes, where a 230 μs negative high-voltage pulse (1500 V) is applied to the outer electrode. The tip of the nozzle is positioned 1–2 cm from the laser beam inside the ringdown cavity. Rotational temperatures

of molecular electronic absorption bands are sensitive to the nozzle position, with typical values ranging from 2 to 20 K.

The new laboratory band is shown in Figure 1 against $\lambda 4428$ observed toward a distant O star (Massey & Thompson 1991), a typical profile of this famous diffuse band, which varies little in width or shape from star to star and even at high resolution shows no evidence of buried rotational structure (T. P. Snow 1999, private communication). We have not yet been able to determine the exact elemental formula or structure of the carrier of the laboratory band, nor have we been able to demonstrate with certainty that the laboratory band is the same as that observed in space. But as Figure 1 emphasizes, the agreement in wavelength between the two is very good (a few parts in 10^4), and the probability of a chance coincidence would seem to be very small because the density of bands as strong as that here (other than from C_2 or C_3) in our benzene spectrum is remarkably low: about 1 per 2000 cm^{-1} .

The carrier of the laboratory band is almost certainly a hydrocarbon. Van der Waals complexes with the inert gas can be produced at very low rotational temperatures in a supersonic expansion, but our band cannot be the result of such a complex because it is independent of the inert gas, being produced with similar intensity and at precisely the same wavelength with both neon and argon. Impurities, too, are unlikely to be the carrier. Although the six-membered rings benzene and toluene are the best precursor molecules, the band has also been found at reduced intensity (by a factor of at least 3) in discharges through four hydrocarbons with linear carbon backbones: allene, methylacetylene, diacetylene, and methyl diacetylene. It is unlikely that the same impurity would appear at comparable abundances with all these precursors. The absence of the band in all discharges studied so far through molecules containing oxygen, nitrogen, silicon, and sulfur is further evidence against an impurity carrier.

The carrier must contain hydrogen as well as carbon, since the band disappears when a fully deuterated precursor is employed (e.g., C_6D_6) and a new band of similar structure and intensity appears 122.8 cm^{-1} to the blue, as shown in Figure 2. A crucial quantitative clue to the number of hydrogen atoms is then provided by partial deuteration. With either

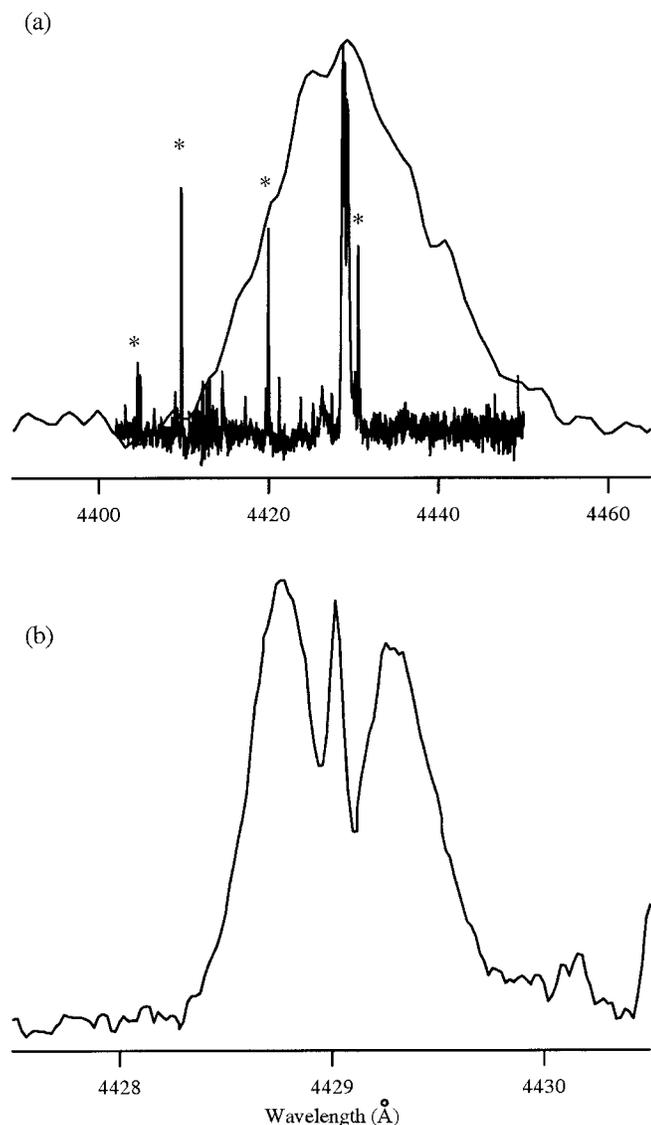


FIG. 1.—(a) New laboratory molecular band, superposed on the diffuse interstellar band $\lambda 4428$ observed toward an O3 If star in the Cyg OB2 association at 1700 pc. (b) The same laboratory band plotted on an expanded wavelength scale, displaying (from right to left) apparent *P*-, *Q*-, and *R*-branches. Features marked by an asterisk denote unassigned lines of light hydrides.

C_6H_5D or C_6HD_5 as precursor, three distinct isotopically shifted bands are observed, two with twice the intensity of the third. These highly specific isotopic spectra are readily interpreted in terms of two pairs of equivalent hydrogen atoms plus a single hydrogen, for a total of five. Two additional facts confirm that this interpretation is almost certainly correct. First, deuterium isotopic shifts of electronic bands are generally additive to an accuracy of a few percent (Garforth, Ingold, & Poole 1948), and that is what is observed (Table 1). Specifically, twice the sum of the shifts of the two strong deuterated bands plus the shift of the weak deuterated band predicts a shift for the totally deuterated species of 120.6 cm^{-1} , only 2% less than the observed shift of 122.8 cm^{-1} . Second, the structure of the isotopic shifts observed with C_6H_5D is almost exactly the mirror image of that observed with C_6HD_5 , as shown in Figure 2. This remarkable symmetry follows naturally from the proposed structure and is quite difficult to explain on the basis of any other.

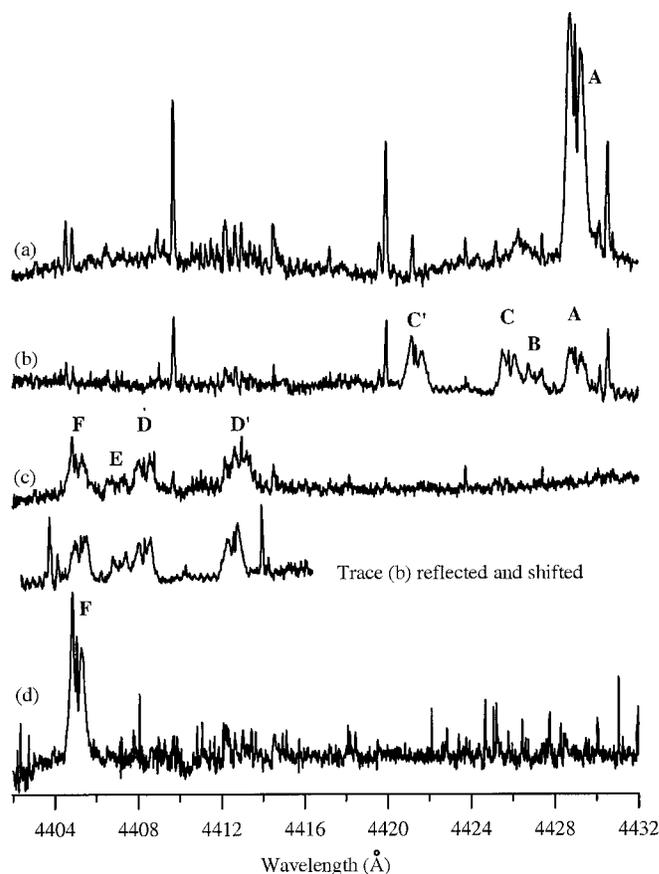


FIG. 2.—Deuterium isotope shifts of the laboratory band at $\lambda 4429$. Trace (a) shows the band A produced with normal benzene, the same as that shown in Fig. 1. Trace (b) shows the three singly deuterated isotopic bands B, C, and C' observed with C_6H_5D , and (c) shows the singly hydrogenated bands D, D', and E observed with C_6HD_5 . Finally, (d) shows the fully deuterated isotopic band F observed with pure C_6D_6 . To a small fraction of the width of each band, the shifts in (c) are the mirror image of those in (b). The intensity ratio of the residual normal band A relative to band B in trace (b) is an interesting question. It would be expected to be five if the hydrogen atoms were randomly shuffled in the discharge prior to formation of the carrier of our band, but would be only one if the carrier were generated by randomly removing one hydrogen (or deuterium) from C_6H_5D . The observed ratio of about two is presumably the result of incomplete shuffling. Similarly for the residual fully deuterated band F in (c).

We conclude that the carrier of laboratory $\lambda 4429$ is very likely a hydrocarbon molecule with the elemental formula C_nH_5 .

The number of carbon atoms n is then the crucial question. One might hope to determine that by ^{13}C substitution similar to that done with deuterium, but the isotopic shifts are unfortunately too small to yield much useful information. With fully ^{13}C -substituted benzene as the precursor gas, we find that $\lambda 4429$ shifts only 5.8 cm^{-1} to the blue—slightly more than the width of the band—which implies that the required shifts of the single ^{13}C isotopomers are too small to resolve or measure with the present signal strength and spectral resolution. Plausible limits on the number of carbon atoms can be set, however. There is no feasible candidate for the carrier with $n = 2$, and one that small in any case is almost certain to possess well-resolved rotational structure in its optical bands. No such structure is observed, however, even in intracavity etalon scans. The finding that the very stable six-membered benzene ring is the best precursor for the band further suggests that n is not likely to be greater than six. This is not a very secure upper limit because

TABLE 1
 OBSERVED BANDS OF LABORATORY $\lambda 4429$ AND ITS DEUTERATED ISOTOPIC SPECIES

Precursor	λ_{air} (\AA)	ν (cm^{-1})	Shift from Normal Band (cm^{-1})	Shift from Deuterated Band (cm^{-1})	Statistical Weight	Weighted Shift (cm^{-1})
C_6H_6	4429.27(4)	22570.8(2)
$\text{C}_6\text{H}_5\text{D}$	4427.32(4)	22580.8(2)	10.0(2)	...	1	10.0(2)
	4426.08(4)	22587.1(2)	16.3(2)	...	2	32.6(4)
	4421.63(4)	22609.8(2)	39.0(2)	...	2	78.0(4)
Sum	120.6(6)
$\text{C}_6\text{D}_5\text{H}$	4407.26(4)	22683.5(2)	...	-10.1(2)	1	-10.1(2)
	4408.56(4)	22676.8(2)	...	-16.8(2)	2	-33.6(4)
	4413.26(4)	22652.7(2)	...	-40.9(2)	2	-81.8(4)
Sum	-125.5(6)
C_6D_6	4405.31(4)	22693.6(2)	122.8(3)

NOTE.—Uncertainties in parentheses are an estimated 1σ in the last significant digit.

reactive molecules as large as HC_{17}N have been detected by Fourier transform microwave spectroscopy in the products of a diacetylene discharge similar to that here (McCarthy et al. 1998)—but it is a reasonable limit to adopt for the time being because we do not find benzene to be a good source for known molecules with more than six carbon atoms (e.g., HC_7H). If ultimately no viable carrier can be found with three to six carbon atoms, ones with still more will obviously have to be considered.

Figure 3 is then a collection of molecules with the requisite number of carbon and hydrogen atoms that are thought to possess two pairs of equivalent H atoms. The phenyl radical I, obtained by removing an H atom from benzene, is an obvious candidate, but it can be rejected because its optical spectrum is well studied (Porter & Ward 1965) and none of its strong bands coincides with $\lambda 4428$ (these strong bands are detectable by CRDS in our benzene discharge, but are quite faint). The allyl radical II suffers the same objection: none of its known

bands falls at $\lambda 4428$ (Currie & Ramsay 1966). However, it is worth noting that one of its stronger bands lies only 1900 cm^{-1} to the blue at $\lambda 4083$. Because allyl is a carbon chain, its strong absorption bands, like those of other chains, might be expected to shift to the red with increasing chain length (Maier 1998), and for that reason we include as a candidate in Figure 3 the hypothetical dimethylene allenyl radical III, about which very little seems to be known. Ab initio calculations by P. v. R. Schleyer (1999, private communication) predict that this radical has a very small dipole moment (only 0.10 D) and that it is about 46 kcal mol^{-1} less stable than the isomeric rearrangement cyclopentadienyl, a radical not included as a candidate in Figure 3 because it—and its aromatic anion as well—are highly symmetrical, possessing essentially D_{5h} symmetry and five equivalent H atoms (Engelman & Ramsay 1970).

Bai & Ault (1992) have shown that fulvene, an isomer of benzene, is abundantly produced in a corona discharge through benzene, and the fulvenyl radical IV, the isomer of phenyl obtained from fulvene by removing one of the H atoms of its CH_2 group, probably has the right symmetry to explain our observations, as Figure 3 shows. To the best of our knowledge, there are no spectroscopic observations of fulvenyl that rule it out. Although less stable than phenyl by about 36 kcal mol^{-1} (1.6 eV) according to an ab initio calculation (P. v. R. Schleyer 1999, private communication), fulvenyl is still stable enough by interstellar standards to deserve consideration.

The carrier of laboratory $\lambda 4429$ might be a positive or negative ion of any of the above candidates. We think it unlikely that the carrier molecule is an anion because we have never detected negative ions among the products of the kind of discharges discussed here—either by optical or microwave spectroscopy. Several cations have been observed, however, and the allyl cation (whose optical spectrum, as far as we can tell, is unknown) is an attractive candidate because it can probably be made in the interstellar gas from the plausibly abundant nonpolar molecule allene via a standard ion-molecule reaction: $\text{C}_3\text{H}_4 + \text{H}_3^+ \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$. By similar reasoning, the dimethylene allenyl cation is also a plausible candidate.

It is difficult to reconcile the apparent *P*-, *Q*-, and *R*-branches in our laboratory band, clearly seen in all the isotopic species in Figure 2, with the oblate molecules I and IV in Figure 3, but it may be possible to do so with the chainlike molecules II and III. If only the lowest *K* ladder is significantly populated in the electronic ground state of these nearly symmetric prolate tops, the observed band will approximate that of a linear molecule with well-defined *P*-, *Q*-, and *R*-branches. With the 50° deviation from linearity calculated ab initio by P. v. R. Schleyer

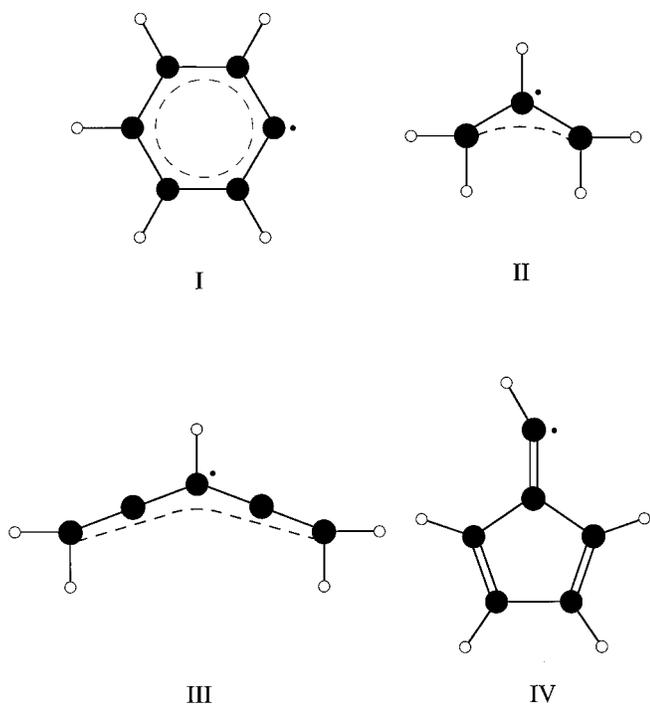


FIG. 3.—Selection of hydrocarbon molecules with the elemental formula C_nH_5 and the right symmetry to explain laboratory $\lambda 4429$.

(1999, private communication), it is difficult to suppress the subbranches that arise from the $K = 1$ and higher rotational ladders if the rotational temperature in our molecular beam is much higher than 2 K. However, it might be possible if the beam is cold and the radical is actually somewhat straighter than calculated, departing from linearity instead by only 20° – 25° . A merit of this interpretation is that at the fairly high rotational temperature (100–200 K) that these weakly polar molecules are likely to have in the diffuse interstellar gas, the many subbands from the higher K ladders of the ground state may fill out nicely the full 63 cm^{-1} wide contour of astronomical $\lambda 4428$.

We have also attempted to find $\lambda 4429$ in our benzene discharge by laser-induced fluorescence, a technique that, when the fluorescence efficiency is high, is generally more sensitive than CRDS. As we recently found for the carbon chains HC_7H and HC_9H (also detected by CRDS: Ball et al. 1999), no fluorescence whatever was observed, the result presumably of either predissociation or radiationless transitions out of the upper electronic state of our band at a rapid rate.

There are several possible ways to decide which of these several candidates—if any—is the carrier of laboratory $\lambda 4429$. Resolution of the rotational structure could provide invaluable information, but unfortunately at the highest resolution of our laser system no structure is apparent. The discovery of vibrational progressions, such as those of C_7^- recently assigned by Tulej et al. (1998) to diffuse bands between 5400 and 6300 Å, could provide vital clues to the number of carbon atoms in the carrier and its structure. A search covering nearly 3500 cm^{-1} to the red of $\lambda 4429$ has yielded no similar bands, suggesting that $\lambda 4429$ is the origin band of the electronic transition being observed. Unfortunately, a preliminary search covering nearly 2400 cm^{-1} to the blue has provided no evidence of a vibronic sequence. Also, spectroscopic detection of our band with mass selection (e.g., by resonance-enhanced multiphoton ionization spectroscopy) could provide a decisive determination of the elemental composition. Finally, microwave-optical double res-

onance detection of our band might also provide conclusive identification of the carrier.

As Figure 1 shows, astronomical $\lambda 4428$ is about 17 times wider than our laboratory band, and this difference must ultimately be explained for a viable identification. We tentatively attribute it to the very low rotational temperature of molecules in our supersonic beam versus the high rotational temperature expected for a nonpolar or weakly polar molecule in the diffuse interstellar gas. To prove that conjecture, however, a great deal must be done or clarified. The specific molecule and type of electronic transition must be determined, and the rotational constants of the upper and lower states of the transition and the orientation of the transition dipole moment must also be ascertained. To calculate the expected band contour of $\lambda 4428$ in space, the permanent electric dipole moment of the lower state may also be required because it affects the rotational excitation of the ground state in the competition between collisional impact ($T = 100$ – 200 K) and radiative excitation ($T = 2.7$ K) if neither predominates.

The astronomical importance of the present detection and analysis obviously depends on whether the band here is the same as that observed in space, a question that is unlikely to be settled until the molecule we are observing in the laboratory is unambiguously identified. If the astronomical and laboratory bands are indeed the same, the present detection should constitute a substantial step toward the solution of the long-standing problem of $\lambda 4428$, one nearly 65 years old (Merrill 1936). The array of laser, mass spectrometric, microwave, and theoretical techniques that can now be brought to bear on a problem of this kind is formidable, so an unambiguous assignment of the carrier of $\lambda 4428$ may now be possible on a fairly short timescale.

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