

Structure, Dynamics and Vibrational Spectra of α -Chloroallyl Cations in Solid SbF_5 -Matrices[†]

Hrvoj Vančik, Zlatko Mihalić,* and Davor Kidemet*

*University of Zagreb, Faculty of Science, Department of Chemistry,
Strossmayerov trg 14, 10000 Zagreb, Croatia*

Received May 31, 1996; accepted August 14, 1996

Cis- and *trans*- α -chloroallyl cations were prepared by matrix isolation method in solid SbF_5 matrix, and obtained FT-IR spectra compared with the results of high-level *ab-initio* calculations. Ionization of either *cis*- or *trans*-1,3-dichloropropenes lead to the mixture of *cis*- and *trans*-cations, whose interconversion barrier is smaller than for parent allyl cation. The extent of α -chlorine carbocation stabilization was shown to be comparable to that obtained by methyl group. Additionally, the ionization constant of chloropropenes in the solid SbF_5 matrix was measured for the first time.

INTRODUCTION

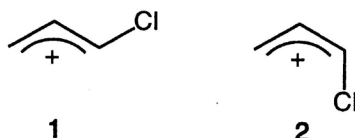
Although a series of allyl cations were investigated in detail by NMR¹ and solvolysis experiments, IR spectra are known for only a few allyl cations. By protonation of cyclohexene derivative, Deno² *et al* succeeded in observing 1,3,5-tetramethylcyclohexenyl cation by IR. The intensive signal at 1533 cm^{-1} was assigned to the C–C–C⁺ stretching vibration of the allyl group. Recent development of a superacid solid matrix method³ enabled us to isolate a series of elusive allyl cations, such as 1-methylallyl,⁴ and even the parent allyl⁵ cation. Both ions can be characterized by the intensive C–C–C⁺ stretching absorbance in the 1550 cm^{-1} region. This frequency is about 100 cm^{-1} lower than the C=C stretching frequency of the corresponding alkene.

[†] Dedicated to the memory of Professor Stanko Borčić.

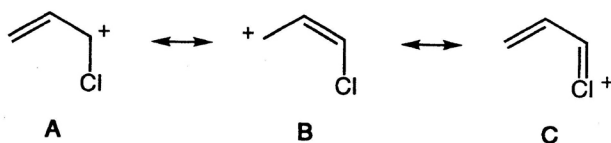
* Authors to whom correspondence should be addressed.

Chlorine as an α -substituent has a stabilizing effect on the allyl group, which can be ascribed to back donation of n-electrons. From previous studies of simple α -chlorocarocations, it is known that the C-Cl stretching frequency is much higher in cations than in the corresponding alkyl chloride precursors (for example, 1045 cm^{-1} in CCl_3^+ ion compared to 780 cm^{-1} in CCl_4).⁶ This frequency shift is a consequence of the significant double bond character of C⁺-Cl bond brought about by interaction with the neighbouring cationic centre.

Distribution of π -electrons in the simplest chloroallyl cations **1** and **2**



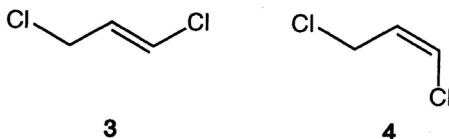
can be described by resonance forms A-C.



While structures **A** and **C** can be rotated about the C1-C2 bond, giving the corresponding *trans*-isomer, structure **B** has a double bond between C1 and C2, and is responsible for the existence of *cis-trans* rotational barrier. Consequently, higher back donation (*i.e.* a higher contribution of structure **C**) results in the C2-C3 double bond localization and a lower rotational barrier. In this work, we wish to present the detailed structure of cations **1** and **2** by *ab initio* calculations and by analysis of their FT-IR spectra. Comparison of these structures with the corresponding methyl substituted allyl cations can, hopefully, provide details on the relative efficiency of methyl and chlorine as stabilizing groups.

EXPERIMENTAL

A commercially available mixture of **3** and **4** was separated by preparative GC in a didecylphthalate $10' \times 3/8''$ column at $90\text{ }^\circ\text{C}$. Retention times were 9.8 min for *cis* and 14.2 min for *trans* isomer. All of the matrix samples were prepared in closed



cycle helium cryostat Leybold-Heraeus ROK 10–300. Approximately 25 mg of the substrate was used. Deposition times were 10–12 min, and the cold window was held at 10 K. The matrix to sample ratio was about 500 : 1. Spectra were recorded on a PE 1725X FT-IR spectrometer with 2 cm^{-1} resolution at different temperatures in the range between 10 and 250 K.

Methods of Calculation

Quantum mechanical *ab initio* calculations were performed by GAMESS (Jan. 1993 version)⁷ and Gaussian 92⁸ packages on MP2(FC) level using the 6-31G* basis set.

RESULTS AND DISCUSSION

Ionization of 1,3-Dichloropropenes

By warming the SbF_5 matrix with deposited precursors **3** or **4** to 150 K, the IR spectra change as it is illustrated in Figures 1 and 2. Signals at 1629 cm^{-1} , assigned to the stretching vibration of C=C bond, disappear. Two new signals at 1564 cm^{-1} and 1558 cm^{-1} appear in both spectra as the most intensive signals in the C=C stretching region. Assignment of these signals to the A' vibration, which includes CCC^+ stretching of the allyl group, is based on comparison with the MP2/6-31G* calculations (Figure 3). Appearance of two signals in both experiments demonstrates that both cations **1** and **2** are present in equilibrium (Figure 4). Calculated A' vibrations are 1673 cm^{-1} for *cis* and 1680 cm^{-1} for *trans* isomer (scaling with factor 0.95 gives 1589 cm^{-1} for *cis* and 1596 cm^{-1} for *trans*). Although calculated (unscaled) values differ from the experimental frequencies, the $\nu_{\text{trans}} - \nu_{\text{cis}}$ difference ($1680 - 1673 = 7\text{ cm}^{-1}$ unscaled, 6 cm^{-1} scaled), is the same as in the experiment ($1564 - 1558 = 6\text{ cm}^{-1}$).

Cis-trans Isomerization

The relatively low rotational barrier implies stabilization of the allyl cations by chlorine n-electrons. Activation energy for the *cis-trans* isomerization, 20.9 kcal/mol, can be calculated from the energies of the fully optimized cations **1**, **2** and the energy of the transition structure **5** (Figure 5). Comparison of rotational barriers in differently substituted allyl cations (Table I) gives us an idea about the magnitude of the stabilizing effect of the corresponding substituents. In the parent allyl cation, the rotational barrier (37.8 kcal/mol)⁹ is almost twice as that in the methyl- or chloro substituted ones. On the other hand, the values obtained for chlorine and the methyl group are very close. It follows that the extent of stabilization of carbocation by the chlorine n-electrons is comparable to the corresponding C–H hyperconjugative stabilization by methyl group.

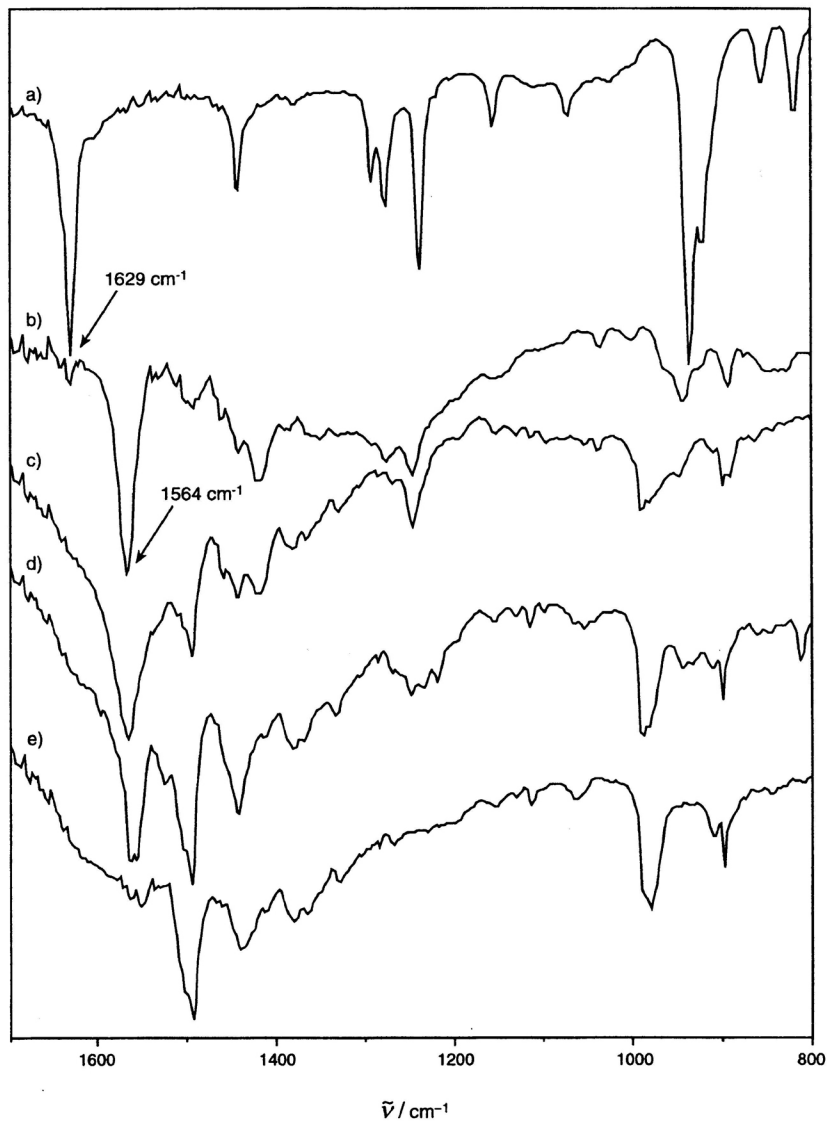


Figure 1. FT-IR spectra of **3** in SbF_5 matrix at b) 77 K, c) 100 K, d) 160 K, e) 220 K.

Kinetics of Ionization

α -Chloroallyl cations have already been studied by kinetic measurements. The solvolysis rates of different chlorinated propenes were measured in diluted formic acid at 100 °C.¹¹ However, data for the ionization in su-

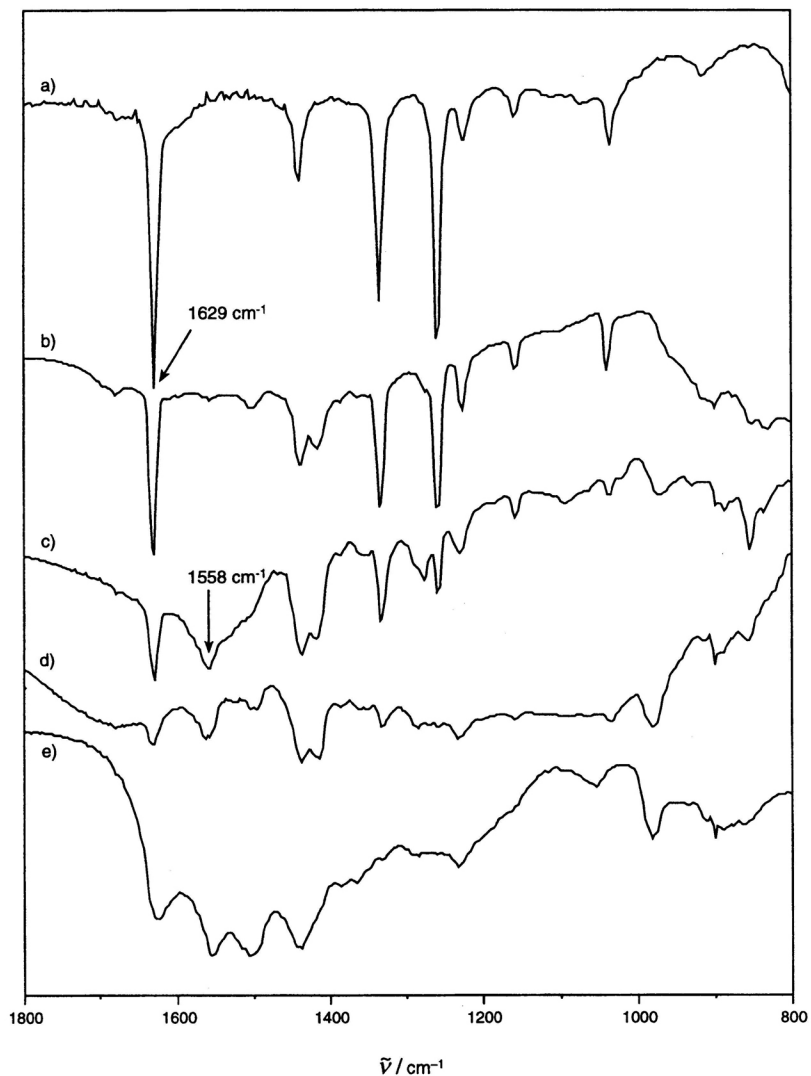


Figure 2. FT-IR spectra of **4** in SbF_5 matrix at b) 77 K, c) 100 K, d) 160 K, e) 220 K.

peracid medium has not been available until now. The relatively high quality of the obtained spectra enabled us to measure the rate of ionization of **3** in the solid superacid matrix. The rate constant was measured at 70 K

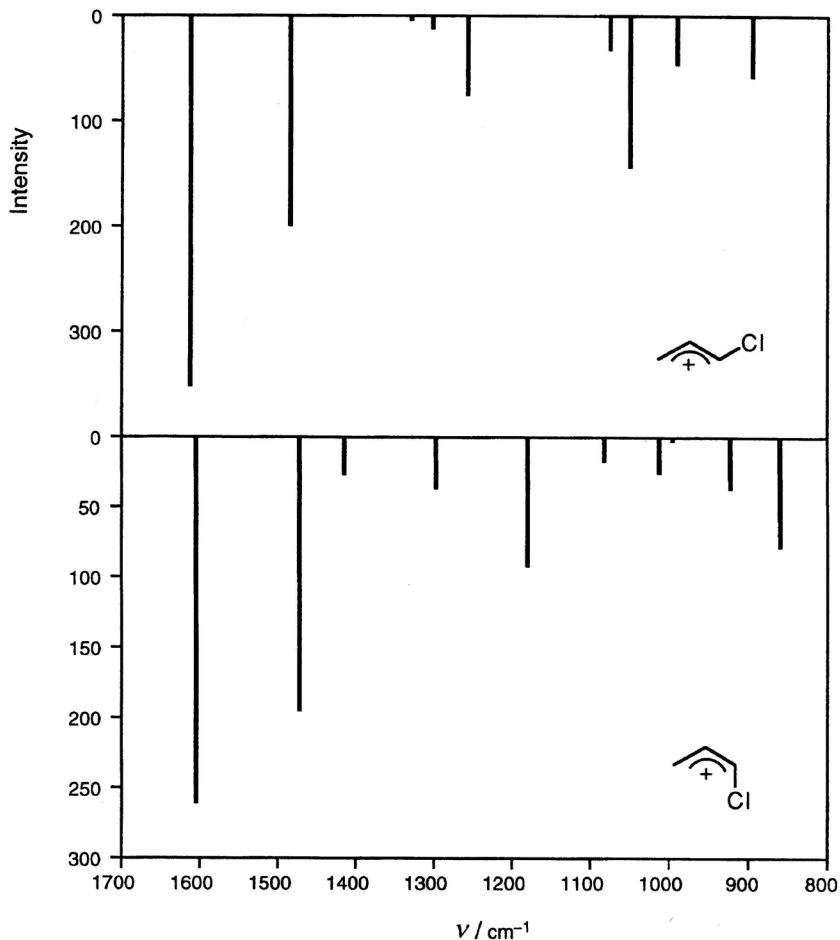


Figure 3. *Ab initio* (MP2(FC)/6-31G*) calculated spectra of **1** and **2**.

by following the disappearance of the signal at 1640 cm^{-1} and simultaneous appearance of the new signal at 1564 cm^{-1} (Figure 6). The resulting values for $k_{\text{ionization}}$ calculated from both sets of spectral data are close, $(4.63 \pm 0.51) \times 10^{-3}\text{ s}^{-1}$ and $(4.03 \pm 0.57) \times 10^{-3}\text{ s}^{-1}$, respectively.

CONCLUSION

Ionization of either *cis*- or *trans*-1,3-dichloropropenes led to a mixture of the corresponding *cis*- and *trans*- α -chloroallyl cations. From the rotational

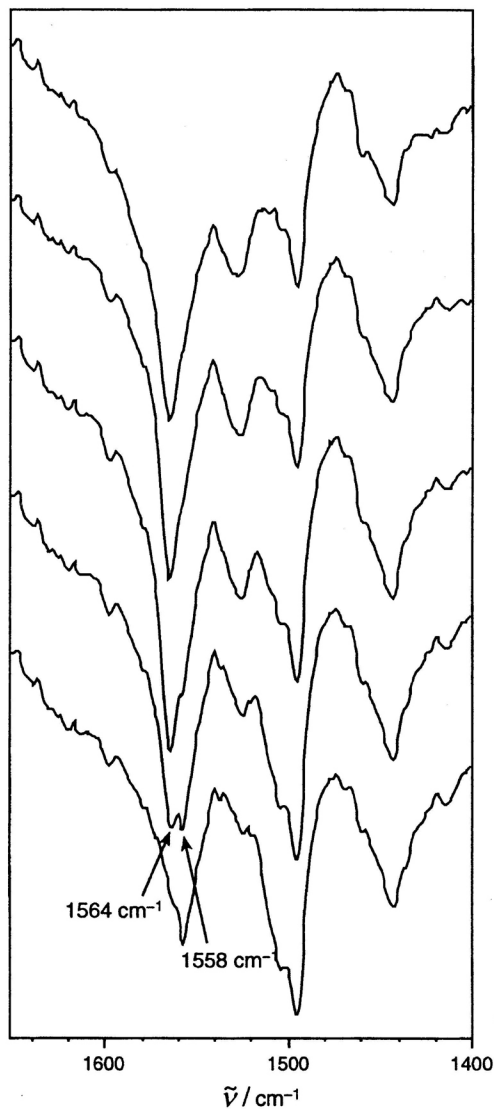


Figure 4. Change of the IR spectra of the mixture of **1** and **2** obtained by ionization of **3**. Labeled signals belong to the CCC^+ stretching vibrations of *cis* and *trans* isomer.

barriers of chloro and methyl-substituted allyl cations it follows that the extent of carbocation stabilization by chlorine *n*-electrons is comparable with that obtained by the methyl group. Additionally, the ionization constant of chloropropenes in the solid SbF_5 matrix was measured for the first time.

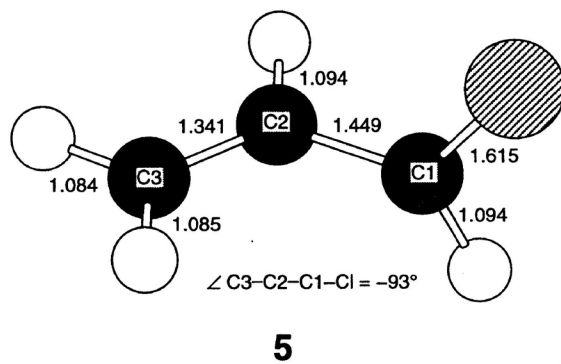
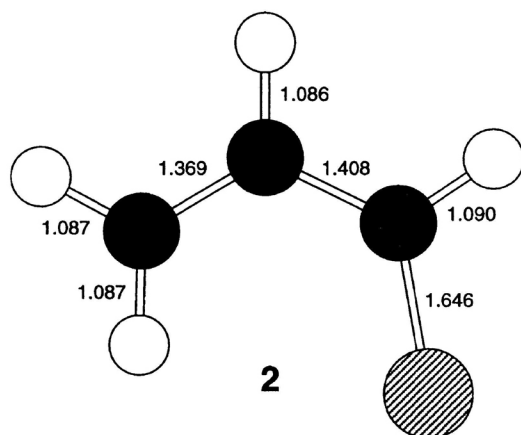
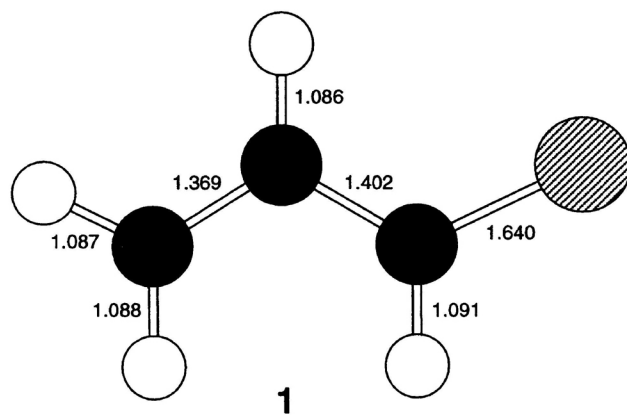
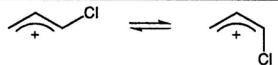
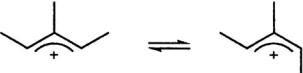
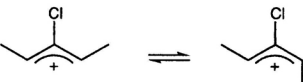
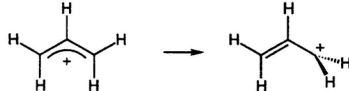
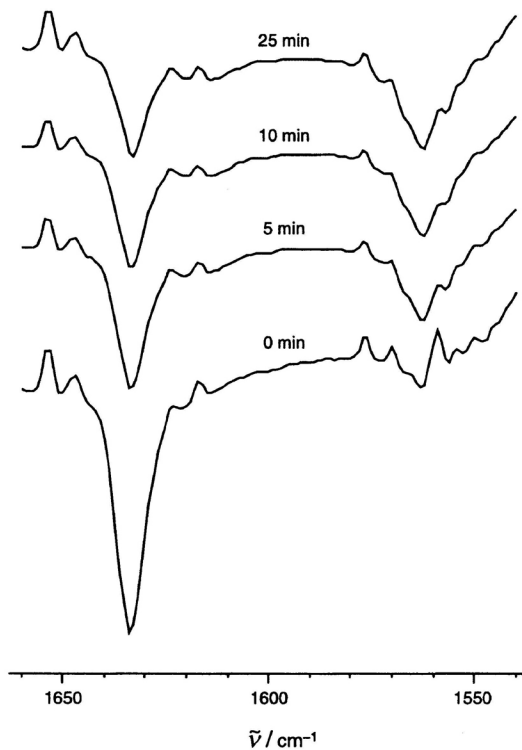


Figure 5. *Ab initio* (MP2/6-31G*) optimized geometries of ions 1, 2 and the transition structure 5.

TABLE I

Comparison of rotational barriers in differently substituted allyl cations¹⁰

	$E_a/\text{kcal mol}^{-1}$	
	20.9	this work
	21.9	Ref. 10
	18.2	Ref. 10
	37.8	Ref. 9

Figure 6. FT-IR spectral change during the ionization of **3** at 70 K.

REFERENCES

1. a) N. C. Deno, in: G. A. Olah and P. von R. Schleyer (Eds.), *Carbonium Ions*, Vol 2, Wiley-Interscience, New York, 1970, Chapter 2.
- b) G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *J. Am. Chem. Soc.* **93** (1971) 4219.
- c) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.* **97** (1975) 1539, 1845.
- d) G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Am. Chem. Soc.* **97** (1975) 5489.
- e) G. A. Olah and H. Mayr, *J. Am. Chem. Soc.* **98** (1976) 7333.
- f) G. A. Olah and H. Mayr, *J. Am. Chem. Soc.* **100** (1978) 6544.
- g) H. Mayr and G. A. Olah, *J. Am. Chem. Soc.* **99** (1977) 510.
- h) *Methoden Org. Chem. (Houben-Weyl)*, 4th ed. 1952, Bd. E19c, 1990.
2. N. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.* **84** (1962) 1498.
3. a) H. Vančik and D. E. Sunko, *J. Am. Chem. Soc.* **111** (1989) 3742.
- b) H. Vančik, *Pure Appl. Chem.* **67** (1995) 761.
4. H. Vančik, V. Gabelica, D. E. Sunko, P. Buzek, and P. von R. Schleyer, *J. Phys. Org. Chem.* **6** (1993) 427.
5. P. Buzek, P. von R. Schleyer, H. Vančik, Z. Mihalić, and J. Gauss, *Angew. Chem., Int. Ed. Engl.* **33** (1994) 448.
6. H. Vančik, K. Percač, and D. E. Sunko, *J. Am. Chem. Soc.* **112** (1990) 7418.
7. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *QCPE Bulletin* **10** (1990) 52.
8. Gaussian 92, Revision D.3, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defress, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA 1992.
9. A. Gobbi and G. Frenking, *J. Am. Chem. Soc.* **116** (1994) 9275.
10. J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Am. Chem. Soc.* **92** (1970) 4025.
11. C. A. Vernon, *J. Chem. Soc.* (1954) 423.

SAŽETAK

Struktura, dinamika i vibracijski spektri α -kloralilnih kationa u čvrstim matricama SbF₅

Hrvoj Vančik, Zlatko Mihalić i Davor Kidemet

Cis- i *trans*- α -kloralilni kationi pripremljeni su tehnikom matrične izolacije u čvrstoj matrici SbF₅. Dobiveni FT-IR spektri uspoređeni su s rezultatima *ab initio* računa visoke razine. Ionizacija *cis*- i *trans*-1,3-diklorpropena daje smjesu *cis*- i *trans*-kloralilnog kationa, čija je barijera interkonverzije manja nego ona alilnog kationa. Stupanj stabilizacije karbokationa α -klorom otprilike je jednak kao u supstituciji metilnom skupinom. Također, po prvi puta su izmjerene konstante ionizacije klorpropena u čvrstoj matrici SbF₅.